A TEXT-BOOK OF
INORGANIC CHEMISTRY
VOLUME XI. PART I

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EDITED BY

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THE PERIODIC TABLE.*

Periods.	Group O.	Group I	Group II	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
		1 H 1·008							
First short period	*2* He 4·00	*3* Li 6·940	*4* Be 9·02	*5* B 10·82	*6* C 12·000	*7* N 14·008	*8* O 16·000	*9* F 19·00	
Second short period	*10* Ne 20·2	*11* Na 22 997	*12* Mg 24·32	*13* Al 26·97	*14* Si 28·06	*15* P 31·027	*16* S 32·064	*17* Cl 35·457	
First long period — Even series	*18* A 39·91	*19* K 39·096	*20* Ca 40·07	*21* Sc 45·10	*22* Ti 48·1	*23* V 50·96	*24* Cr 52·01	*25* Mn 54·93	*26* Fe 55·84 / *27* Co 58·94 / *28* Ni 58·69
First long period — Odd ,,		*29* Cu 63·57	*30* Zn 65·38	*31* Ga 69·72	*32* Ge 72·60	*33* As 74·96	*34* Se 79·2	*35* Br 79·916	
Second long period — Even series	*36* Kr 82·9	*37* Rb 85·44	*38* Sr 87·63	*39* Y 88·9	*40* Zr 91·0	*41* Nb 93·1	*42* Mo 96·0	*43* ...	*44* Ru 101·7 / *45* Rh 102·91 / *46* Pd 106·7
Second long period — Odd ,,		*47* Ag 107·880	*48* Cd 112·41	*49* In 114·8	*50* Sn 118·70	*51* Sb 121·77	*52* Te 127·5	*53* I 126·932	
Third long period	*54* X 130·2	*55* Cs 132·81	*56* Ba 137·37	*57* La 138·90	*58* Ce 140·25 / *59* Pr 140·92	*60* Nd 144·27 / *61* ..	*62* Sm 150·43 / *63* Eu 152·0	*64* Gd 157·26 / *65* Tb 159·2	
Fourth long period		*66* Dy 162·52 / *67* Ho 163·4	*68* Er 167·7 / *69* Tm 169·4	*70* Yb 173·6 / *71* Lu 175·0	*72* Hf [180·8]	*73* Ta 181·5	*74* W 184·0	*75* ...	*76* Os 190·8 / *77* Ir 193·1 / *78* Pt 195·23
Fifth long period — Even series		*79* Au 197·2	*80* Hg 200·61	*81* Tl 204·39	*82* Pb 207·20	*83* Bi 209·00	*84* Po [210]	*85* ...	
Fifth long period — Odd ,,	*86* Rn 222	*87* ...	*88* Ra 225·95	*89* Ac ...	*90* Th 232·15	*91* Pa ...	*92* U 238·17		
Volume in this series of text-books.	1	2	3	4	5	6	7	8	9

* The International Atomic Weights for 1925 are adopted in this Table.

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EDITED BY

J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,

CARNEGIE GOLD MEDALLIST.

VOLUME XI.

ORGANOMETALLIC COMPOUNDS.

PART I.

DERIVATIVES OF THE ELEMENTS OF GROUPS I TO IV.

BY

ARCHIBALD EDWIN GODDARD, M.Sc. (B'ham), A.I.C.,

AND

DOROTHY GODDARD, M.Sc. (B'ham).

LONDON:

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GENERAL INTRODUCTION TO THE SERIES.

DURING the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group O, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are

subjects of supreme importance to the student of Inorganic Chemistry and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the Elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX. under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicles and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

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Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing to the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

Hydrogen	= 1·00762.	Oxygen	= 16·000.
Sodium	= 22·996.	Sulphur	= 32·065.
Potassium	= 39·100.	Fluorine	= 19·015.
Silver	= 107·880.	Chlorine	= 35·457.
Carbon	= 12·003.	Bromine	= 79·916.
Nitrogen	= 14·008.	Iodine	= 126·920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive,

as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xvii–xix.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi–xxviii) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

September 1928.

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PREFACE.

THE present book aims at giving a tolerably complete account of the preparation and properties of the organic compounds of the elements of Groups I. to IV. of the Periodic Classification. Except in the case of mercury, no monograph has appeared in any language which deals with the organic compounds derived from the elements of these groups. The term *organometallic* as used in this volume is applied only to compounds containing a second element directly linked to carbon, and excludes those where the element is linked *via* oxygen or nitrogen, as well as double compounds of organic substances with inorganic salts. In spite of these omissions, the present volume gives an account of approximately 2300 compounds. In order to make the book as complete as possible, the preparation of all *key* compounds has been given in detail, and it may be used as a treatise on practical organic chemistry. Since it has been necessary to cover so much ground no systematic attempt has been made to enter into theoretical aspects of the subject, but by endeavouring to include all known compounds chemists will be able to make valuable comparisons of the compounds of the various elements, which was hitherto impossible without consulting a vast amount of original literature. To make the text more readable, physical constants of large series of compounds have been placed in the Appendix, and throughout the book greater attention has been paid to physical properties generally than is usual in this type of book. The Authors' experience has shown that such data would have been very useful in their own research work if it had been available in book form.

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In conclusion, the Authors wish to thank the Editor, Dr. J. Newton Friend, for his invaluable help in reading the whole of the manuscript and proofs, to Messrs. Flack and Smith of the Library of the University of Birmingham, for giving the Authors free access to any portion of the Library, and to E. Masters, B.Sc., A.R.C.S., for lending the Authors his copies of the *Journal* of the American Chemical Society. Reprints of original papers dealing with organometallic compounds will be thankfully received by the Authors.

A. E. GODDARD.
D. GODDARD.

September 1928.

CONTENTS.

PAGE

THE PERIODIC TABLE. (*Frontispiece*) iv

GENERAL INTRODUCTION TO THE SERIES vii

PREFACE xi

LIST OF ABBREVIATIONS xvii

TABLE OF DATES OF ISSUE OF JOURNALS xxi

CHAPTER I. **Organometallic Derivatives of the Elements of Group I.** 3

General — Lithium — Sodium — Potassium — Rubidium — Cæsium — Copper —Silver—Gold.

CHAPTER II. **Organometallic Derivatives of the Elements of Group II.** 11

General—Calcium—Beryllium—Magnesium—Zinc—Cadmium.

CHAPTER III. **Mercury** 29

ALKYL COMPOUNDS OF THE TYPES R_2Hg AND RHgX—General—Methyl Compounds—Ethyl Compounds—Propyl Compounds—Butyl Compounds—Amyl Compounds—Heptyl Compounds—Octyl Compounds—Methylmercuric Compounds—Ethylmercuric Compounds—Propylmercuric Compounds —Butylmercuric Compounds—Amylmercuric Compounds—Hexylmercuric Compounds—Heptylmercuric Compounds—Octylmercuric Compounds— —Alkylmercuric Compounds — Propargylmercuric Compounds — Mercury Derivatives of Methylene Iodide.

CHAPTER IV. **Mercury** (*continued*) 47

DERIVATIVES OF ALIPHATIC ALCOHOLS, ALDEHYDES, AND KETONES—General— Ethyl alcohol — Allyl alcohol — Acetaldehyde — Acetone — Methylethyl Ketone.

CHAPTER V. **Mercury** (*continued*) 58

DERIVATIVES OF ALIPHATIC ACIDS—Formic Acid—Acetic Acid—Cyanoacetic Acid—Benzoylacetic Acid—Nitro-acetic Esters—Substituted Acetic Acids— Propionic Acid—Malonic Acid and its Esters—Unsaturated Acids—Acrylic Acid—Crotonic Acid—Maleic Acid—Itaconic Acid—Citraconic Acid— Chaulmoogric Acid and its Ethyl Ester.

CHAPTER VI. **Mercury** (*continued*) 69

AROMATIC COMPOUNDS OF THE TYPES R_2Hg; RHgR′; RHgX—General— Phenyl Compounds—Tolyl Compounds—Benzyl Compounds—Xylyl Compounds—Higher Benzene Homologues—Cyclohexyl Compounds—Diphenyl Derivatives—Naphthyl Derivatives—Thiophene Compounds—Mixed Alkyl-Aryl Compounds—Mixed Diaryl Compounds—Phenylmercuric Compounds —Compounds of Di(phenylmercuri)-amine—Tolylmercuric Compounds— Benzylmercuric Compounds—Compounds from Higher Benzene Homologues—Cyclohexylmercuric Compounds—Naphthylmercuric Compounds— Thienyl Compounds — Dihydronaphthalene Compounds — Halogenated Phenylmercuric Compounds—Derivatives of Nitrobenzene—Derivatives of Nitrotoluenes—Derivatives of Aromatic Sulphonic Acids.

PAGE

CHAPTER VII. Mercury (*continued*) 110

DERIVATIVES OF AROMATIC AMINES—General—Aniline—Halogenated Anilines—Nitroanilines—Mono- and Di-Alkylanilines—Benzylaniline—Acid Anilides—Diphenylamine—α-Anilido-Fatty Acids and their Esters—Tolylglycine Esters—Toluidines and Toluidides—Benzidine—Naphthylamines and their Sulphonic Acids.

CHAPTER VIII. Mercury (*continued*) 136

DERIVATIVES OF AROMATIC COMPOUNDS CONTAINING HYDROXYL GROUPS—General—Phenol—Anisole — Phenetole — Nitrophenols — Aminophenols — Cresols — Thymol — Carvacrol — Alkyl Phenols — Guaiacol — Safrol — —Eugenol Methyl Ether — Resorcinol — Naphthols and their Sulphonic Acids—Salicylyl Alcohol (Saligenin)—*p*-Hydroxy-*m*-Nitrophenyl Carbinol.

CHAPTER IX. Mercury (*continued*) 160

DERIVATIVES OF AROMATIC ACIDS—General—Benzoic Acid and its Esters—Thiolbenzoic Acid—Nitrobenzoic Acids—Salicylic Acid and its Esters—Nitrosalicylic Acid—Anthranilic Esters—Substituted Anthranilic Esters—*m*-Aminobenzoic Acid—*p*-Aminobenzoic Acid and its Esters—Cinnamic Acid and its Esters—β-Hydroxynaphthoic Acid.

CHAPTER X. Mercury (*continued*) 180

MISCELLANEOUS MERCURY DERIVATIVES OF ORGANIC COMPOUNDS—Derivatives of Olefines—Compounds from Acetylene and Phenylacetylene—Derivatives of Cyclo- and Dicyclo-Pentadiene—Allyl and Aryl Mercuric Alkyl Xanthates—Derivatives of Substituted Aryloxy-Fatty Acids—Derivatives of Hydrazines —Derivative of Pyrimidine—Derivatives of Salicyl and Nitrosalicyl Aldehydes—Derivatives of *m*- and *p*-Hydroxy-benzaldehydes and their Nitro-Compounds—Derivatives of Acetophenone—Derivatives of Benzophenone—Derivatives of Indandione and Oxindone—Derivatives of Camphor, Camphor-Carboxylic Acid, Camphene—Derivatives of Terpineol and Dimethyl-heptenol, Allyl Acetoxime, Methylheptenone Oxime, Ethylhexenol—Derivatives of Azo Compounds—Derivatives of Hydroxyazobenzenes—Derivatives of Methylene Blue—Derivatives of Phthaleins—Cyclomercuri-polymethylenes — Derivatives of the Pyrazolone Group — Derivatives of Pyridine—Derivatives of Furane and Pyrrole—Derivatives of the Indole Series—Derivatives of Quinoline—Derivatives of Dihydrobenzofuranes—Derivatives containing Mercury and Selenium.

CHAPTER XI. Organometallic Derivatives of the Metals of Group III. 219

General—Boron : Alkyl Compounds of the Types R_3B, $R_2B.OH$, $RB(OH)_2$—Aryl Compounds of the Types R_3B, R_2BX, RBX_2, $R_2B.OH$, $RB(OH)_2$, RBO.

Aluminium : Alkyl Compounds of the Types R_3Al, R_2AlX, $RAlX_2$—Aluminium Trialkyl Etherates—Compounds from Methylene Iodide—Aryl Compounds of the Type R_3Al.

Indium : Indium Diphenyl Chloride, Indium Phenyl Oxide.

Thallium : Alkyl Derivatives of the Type R_2TlX, Aryl Derivatives of the Type R_2TlX.

CHAPTER XII. Organometallic Derivatives of the Metals of Group IV. 246

General—Silicon : Alkyl Derivatives of the Types R_4Si, R_3SiR', R_2SiR_2', $R_2SiR'R''$, R_3SiX, R_2SiX_2, $RSiX_3$, $R_3Si(OH)$, $R_3Si(OR)$, $R_2Si(OR)_2$, $R_2Si(OR)Hal.$, $RSi(OR)_3$, $Si(OR)_2Hal.$, $(R_3Si)_2O$. R_2SiO, $R.SiO.OH$, $R_3Si.SiR_3$—Aromatic Derivatives of the Types R_4Si, R_3SiX, R_2SiX_2, $RSiX_3$, $R_3Si(OH)$, $R_2Si(OH)_2$, $(RSiO)_2O$, R_2SiO, $(R_3Si)_2O$, $R_2Si(CH_2)_5$, $RSiO_2H$, $RSi(OEt)_3$, $Si(OR^1)(OR^2)(OR^3)(OR^4)$, $XSi(OR^1)(OR^2)(OR^3)$, $X_2Si(OR^1)(OR^2)$, $R_3Si.SiR_3$, $R^1R^2R^3Si.SiR^1R^2R^3$, Si_4Ph_8, $[SiPh_2]_n$—Silicon Compounds containing Lead, Tin, and Arsenic.

Germanium : Alkyl Derivatives of Type R_4Ge, Aryl Compounds of the Type R_4Ge and their Derivatives, Aryl Germanic Acid Anhydrides.

PAGE

CHAPTER XIII. Organometallic Derivatives of Tin . 300

General—Alkyl Derivatives of the Types R_4Sn, R_3SnR', R_2SnR_2', $R_2SnR'R''$, R_3SnX, $R_2R'SnX$, $RR'SnX_2$, $R'R''R'''SnX$, R_2SnX_2, $R.SnO.OH$, $RSnX_3$, R_2Sn, R_3Sn. $R_3Sn.SnR_3$—Aryl Derivatives of the Types R_4Sn, Ar_3SnAr', Ar_3SnAlk, $AlkAlk'SnAr_2$, $AlkAlk_2'SnAr$, Alk_2SnAr_2, Alk_3SnAr, R_3SnX. R_2SnX_2, R_2SnXX', $AlkArSnX_2$. R_2Sn, $Ar_3Sn.SnAr_3$, $Ar_3Sn.SnAlk_3$, R_3Sn, $R_2Sn{<}(CH_2)_5$, Derivatives containing Tin and Lead.

CHAPTER XIV. Organometallic Derivatives of Lead . 332

General—Alkyl Derivatives of the Types R_4Pb, R_3PbR', R_2PbR_2', $R_2PbR'R''$, $RR'R''R'''Pb$, R_3PbX, R_2PbX_2, $R_2PbX'X''$, $RR'PbX_2$, R_3Pb—Aryl Derivatives of the Types R_4Pb, R_3PbR', R_2PbR_2', Alk_3PbAr, Alk_2PbAr_2, R_3PbX, R_2PbX_2, R_2Pb, R_3Pb, $Ar_2AlkPbX$, $Ar_2Ar'PbX$, Ar_3PbAlk, $Ar_2Ar'PbAlk$, $ArAr'PbAlkX$, $R_2Pb{<}(CH_2)_5$.

APPENDIX 356

NAME INDEX 380

SUBJECT INDEX 385

PATENT INDEX 418

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LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
Afhandl. Fys. Kem.	Afhandlingat i Fysik, Kemi och Mineralogi.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim.	Annales de Chimie (1719–1815, and 1914+).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris) (1816–1913).
Ann. Mines	Annales des Mines.
Ann. Pharm.	Annalen der Pharmacie (1832–1839).
Ann. Phys. Chem.	Annalen der Physik und Chemie (1819–1899).
Ann. Physik	Annalen der Physik (1799–1818, and 1900+).
Ann. Physik, Beibl.	Annalen der Physik, Beiblättes.
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbeiten Kaiserl. Gesundheitsamte	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
Arch. exp. Pathol. Pharmak.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles, Genève.
Atti Acc. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia Lincei.
B.A. Reports	British Association Reports.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Akad. Ber.	See *Sitzungsber. K. Akad. Wiss. Berlin.*
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bot. Zeit.	Botanische Zeitung.
Bul. Soc. Stünte Cluj.	Buletinul Societâtel de Stünte din Cluj.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin International de l'Académie des Sciences de Cracovie.
Bull. de Belg.	Bulletin de la Société chimique Belgique.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. min. de France	Bulletin de la Société minéralogique de France.
Bull. U.S. Geol. Survey	Bulletins of the United States Geological Survey.
Centr. Min.	Centralblatt für Mineralogie.
Chem. Ind.	Die Chemische Industrie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung (Cöthen).
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
Crell's Annalen	Chemische Annalen für die Freunde der Naturlehre, von L. Crelle.
Dingl. poly. J.	Dingler's polytechnisches Journal.

Abbreviated Title.	Journal.
Drude's Annalen	Annalen der Physik (1900–1906).
Electroch. Met. Ind.	Electrochemical and Metallurgical Industry.
Eng. and Min. J.	Engineering and Mining Journal.
Gazzetta	Gazzetta chimica italiana.
Gehlen's Allg. J. Chem.	Allgemeines Journal der Chemie.
Geol. Mag.	Geological Magazine.
Gilbert's Annalen	Annalen der Physik (1799–1824).
Giorn. di Scienze Naturali ed Econ.	Giornale di Scienze Naturali ed Economiche.
Helv. Chim. Acta	Helvetica Chim. Acta.
Int. Zeitsch. Metallographie	Internationale Zeitschrift für Metallographie.
Jahrb. kk. geol. Reichsanst.	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
Jahrb. Miner.	Jahrbuch für Mineralogie.
Jahresber.	Jahresbericht über die Fortschritte der Chemie.
Jenaische Zeitsch.	Jenaische Zeitschrift für Naturwissenschaft.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Gasbeleuchtung	Journal für Gasbeleuchtung.
J. Geology	Journal of Geology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Metals	Journal of the Institute of Metals.
J. Miner. Soc.	Mineralogical Magazine and Journal of the Mineralogical Society.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physique	Journal de Physique.
J. prakt. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (*Petrograd*).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Mém. Paris Acad.	Mémoirs présentés par divers savants à l'Académie des Sciences de l'Institut de France.
Mem. Coll. Sci. Kyōtō.	Memoirs of the College of Science, Kyōtō Imperial University.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. scient.	Moniteur scientifique.
Münch. Med. Wochenschr.	Münchener Medizinische Wochenschrift.
Nature	Nature.
Nuovo Cim.	Il nuovo Cimento.
Oesterr. Chem. Zeit.	Oesterreichische Chemiker-Zeitung.
Öfvers. K. Vet.-Akad. Forh.	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Post	Pharmazeutische Post.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Review	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Pogg. Annalen	Poggendorff's Annalen der Physik und Chemie (1824–1877).
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Phil. Soc. Glasgow	Proceedings of the Royal Philosophical Society of Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.

Abbreviated Title.	Journal.
Rec. Trav. chim.	Recueil des Travaux chimiques des Pay-Bas et de la Belgique.
Roy. Inst. Reports	Reports of the Royal Institution.
Schweigger's J.	Journal für Chemie und Physik
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich-Preussischen Akademie de Wissenschaften zu Berlin.
Sitzungsber. K. Akad. Wiss. Wien	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
Techn. Jahresber.	Jahresbericht über die Leistungen der Chemischen Technologie.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Chem. Soc.	Transactions of the Chemical Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trav. et Mèm. du Bureau intern. des Poids et Mes.	Travaux et Mémoires du Bureau International des Poids et Mesures.
Verh. Ges. deut. Naturforsch. Aerzte.	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wied. Annalen	Wiedemann's Annalen der Physik und Chemie (1877–1899).
Wissenschaftl. Abhandl. phys.-tech. Reichsanst.	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem.	Kritische Zeitschrift für Chemie.
Zeitsch. Chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genuss-m.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik, und Photochemie.

DropBooks

TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer. J. Sci.	Ann. Chim. Phys.	Ann. Min.	Arch. Pharm.	Dingl. Poly. J.	Gilbert's Annalen.	J. Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.
1800	...	(1) 32–35	...	...	...	4–6	...	5–8	90	...
1	...	36–39	...	...	...	7–9	...	8–11	91	...
2	...	40–43	...	...	...	10–12	...	11–14	92	...
3	...	44–47	...	...	...	13–15	...	14–17	93	...
4	...	48–51	...	...	...	16–18	...	17–20	94	...
1805	...	52–55	...	...	...	19–21	...	20–23	95	...
6	...	56–60	...	...	...	22–24	...	23–26	96	...
7	...	61–64	...	...	...	25–27	...	26–29	97	...
8	...	65–68	...	...	...	28–30	...	29–32	98	...
9	...	69–72	...	...	...	31–33	(1) 1*	33, 34	99	...
1810	...	73–76	...	...	...	34–36	2	35, 36	100	...
11	...	77–80	...	...	...	37–39	3	37, 38	101	...
12	...	81–84	...	...	...	40–42	4	39, 40	102	...
13	...	85–88	...	...	...	43–45	5	41, 42	103	...
14	...	89–92	...	...	...	46–48	6	43, 44	104	...
1815	...	93–96	...	...	...	49–51	(2) 1	45, 46	105	...
16	...	(2) 1–3	...	...	...	52–54	2	47, 48	106	...
17	...	4–6	1, 2	...	...	55–57	3	49, 50	107	...
18	...	7–9	3	...	...	58–60	4	51, 52	108	...
19	(1) 1	10–12	4	...	...	61–63	5	53, 54	109	...
1820	2	13–15	5	...	1–3	64–66	6	55, 56	110	...
21	3	16–18	6	...	4–6	67–69	7	57, 58	111	...
22	4, 5	19–21	7	1, 2	7–9	70–72	8	59, 60	112	...
23	6	22–24	8	3–6	10–12	73–75	9	61, 62	113	...
24	7, 8	25–27	9	7–10	13–15	76	10	63, 64	114	1, 2
1825	9	28–30	10, 11	11–14	16–18	Continued as Pogg. Annalen.	11	65, 66	115	3–5
26	10, 11	31–33	12, 13	15–19	19–22		12	67, 68	116	6–8
27	12	34–36	(2) 1, 2	20–23	23–26		13	(2) 1, 2	117	9–11
28	13, 14	37–39	3, 4	24–26	27–30		14	3, 4	118	12–14
29	15, 16	40–42	5, 6	27–30	31–34		15	5, 6	119	15–17

* First series known as *Bulletin de Pharmacie.*

Year.	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon.* scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
1830	17, 18	...	43–45	7–8	31–34	...	...	35–38	16	...	...	7, 8	120	18–20	...	...	...
31	19, 20	...	46–48	...	35–39	...	...	39–42	17	...	...	9, 10	121	21–23	...	...	...
32	21, 22	1–4	49–51	(3) 1, 2	40–43	...	...	43–47	18	...	...	11 (3) 1	122	24–26	1	...	...
33	23, 24	5–8	52–55	3, 4	44–47	...	...	48–50	19	...	...	2, 3	123	27–30	2	...	...
34	25–27	9–12	56–57	5, 6	48–50	...	...	51–54	20	1–3	...	4, 5	124	31–33	...	...	...
1835	28, 29	13–16	58–60	7, 8	(2) 1–4	...	1	55–58	21	4–6	...	6, 7	125	34–36	...	...	...
36	30, 31	17–20	61–63	9, 10	5–8	...	2, 3	59–62	22	7–9	...	8, 9	126	37–39	...	...	...
37	32, 33	21–24	64–66	11, 12	9–12	...	4, 5	63–66	23	10–12	...	10, 11	127	40–42	3	...	...
38	34, 35	25–28	67–69	13, 14	13–16	...	6, 7	67–70	24	13–15	...	12, 13	128	43–45	...	...	...
39	36, 37	29–32	70–72	15, 16	17–20	...	8, 9	71–74	25	16–18	...	14, 15	129	46–48	...	...	...
1840	38, 39	*33–36	73–75	17, 18	21–24	...	10, 11	75–78	26	19–21	...	16, 17	130	49–51	...	...	...
41	40, 41	37–40	(3) 1–3	19, 20	25–28	...	12, 13	79–82	27	22–24	...	18, 19	131	52–54	...	...	...
42	42, 43	41–44	4–6	(4) 1, 2	29–32	...	14, 15	83–86	(3) 1, 2	25–27	...	20, 21	132	55–57	...	...	...
43	44, 45	45–48	7–9	3, 4	33–36	...	16, 17	87–90	3, 4	28–30	...	22, 23	133	58–60	4	...	...
44	46, 47	49–52	10–12	5, 6	37–40	...	18, 19	91–94	5, 6	31–33	...	24, 25	134	61–63	...	...	...
1845	48–50	53–56	13–15	7, 8	41–44	...	20, 21	95–98	7, 8	34–36	...	26, 27	135	64–66	...	...	...
46	(2) 1, 2	57–60	16–18	9, 10	45–48	...	22, 23	99–102	9, 10	37–39	...	28, 29	136	67–69	...	...	...
47	3, 4	61–64	19–21	11, 12	49–52	...	24, 25	103–106	11, 12	40–42	...	30, 31	137	70–72	...	1	...
48	5, 6	65–68	22–24	13, 14	53–56	...	26, 27	107–110	13, 14	43–45	...	32, 33	138	73–75	...	1, 2	1
49	7, 8	69–72	25–27	15, 16	57–60	...	28, 29	111–114	15, 16	46–48	...	34, 35	139	76–78	...	2, 3	2, 3
1850	9, 10	73–76	28–30	17, 18	61–64	...	30, 31	115–118	17, 18	49–51	...	36, 37	140	79–81	...	3	4, 5
51	11, 12	77–80	31–33	19, 20	65–68	...	32, 33	119–122	19, 20	52–54	...	(4) 1, 2	141	82–84	5	4	6, 7
52	13, 14	81–84	34–36	(5) 1, 2	69–72	...	34, 35	123–126	21, 22	55–57	...	3, 4	142	85–87	...	5	8, 9
53	15, 16	85–88	37–39	3, 4	73–76	...	36, 37	127–130	23, 24	58–60	...	5, 6	143	88–90	...	6	10, 11
54	17, 18	89–92	40–42	5, 6	77–80	...	38, 39	131–134	25, 26	61–63	...	7, 8	144	91–93	6, 7	7	12–14
1855	19, 20	93–96	43–45	7, 8	81–84	...	40, 41	135–138	27, 28	64–66	...	9, 10	145	94–96	7	8	15–18
56	21, 22	97–100	46–48	9, 10	85–88	...	42, 43	139–142	29, 30	67–69	...	11, 12	146	97–99	8	9	19–22
57	23, 24	101–104	49–51	11, 12	89–92	...	44, 45	143–146	31, 32	70–72	(1) 1	13, 14	147	100–102	9	10	23–27
58	25, 26	105–108	52–54	13, 14	93–96	1	46, 47	147–150	33, 34	73–75	2	15, 16	148	103–105	9	11	28–33
59	27, 28	109–112	55–57	15, 16	97–100	1	48, 49	151–154	35, 36	76–78	3	17, 18	149	106–108	9, 10	12	34–38

* Often referred to by Series: Series 3, vols. 1–16, 1871–1886; Series 4, vols. 1–24, 1887–1910; Series 5, vols. 1–9, 1911–1919 (one vol. yearly).

DropBooks

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Zeit.
1860	...	29, 30	...	113–116	...	58–60	17, 18	101–104	...	2	1, 2	...	...
61	...	31, 32	...	117–120	1	61–63	19, 20	105–108	...	3	3, 4	...	...
62	...	33, 34	...	121–124	2	64–66	(6) 1, 2	109–112	...	4	5, 6	...	...
63	...	35, 36	...	125–128	2	67–69	3, 4	113–116	...	5	7, 8	...	...
64	...	37, 38	...	129–132	3	(4) 1–3	5, 6	117–120	...	(2) 1, 2	9, 10	...	...
1865	...	39, 40	...	133–136	3, 4	4–6	7, 8	121–124	...	3, 4	11, 12	...	...
66	...	41, 42	...	137–140	4	7–9	9, 10	125–128	...	5, 6	13, 14	...	...
67	...	43, 44	...	141–144	5	10–12	11, 12	129–132	...	7, 8	15, 16	...	...
68	...	45, 46	...	145–148	6	13–15	13, 14	133–136	1	9, 10	17, 18	...	...
69	...	47, 48	...	149–152	...	16–18	15, 16	137–140	2	11, 12	19, 20	...	...
1870	...	49, 50	...	153–156	7	19–21	17, 18	141–144	3	13, 14	21, 22	...	...
71	...	(3) 1, 2	...	157–160	...	22–24	19, 20	145–148	4	15, 16	23, 24	...	...
72	..	3, 4	...	161–164	8	25–27	(7) 1, 2	149–150, 201 *	5	17, 18	25, 26	...	...
73	...	5, 6	...	165–170	...	28–30	3, 4	201–203	6	19, 20	27, 28	...	...
74	...	7, 8	...	171–174	.	(5) 1–3	5, 6	204, 205	7	21, 22	29, 30	...	...
1875	...	9, 10	...	175–179	...	4–6	7, 8	206, 207	8	23, 24	31, 32	...	...
76	...	11, 12	1	180–183	...	7–9	9, 10	208, 209	9	25, 26	33, 34	...	...
77	...	13, 14	2	184–189	...	10–12	11, 12	210, 211	10	27, 28	35, 36	...	1
78	...	15, 16	3	190–194	...	13–15	13, 14	212, 213	11	29, 30	37, 38	...	2
79	1	17, 18	4	195–199	...	16–18	15, 16	214, 215	12	31, 32	39, 40	...	3
1880	1, 2	19, 20	5	200–205	...	19–21	17, 18	216, 217	13	33, 34	41, 42	...	4
81	2, 3	21, 22	6	206–210	...	22–24	19, 20	218, 219	14	35, 36	43, 44	...	5
82	3, 4	23, 24	7	211–215	...	25–27	(8) 1, 2	220	15	37, 38	45, 46	...	6
83	4, 5	25, 26	8	216–221	...	28–30	3, 4	221	16	39, 40	47, 48	...	7
84	5, 6	27, 28	9	222–226	...	(6) 1–3	5, 6	222	17	41, 42	49, 50	...	8
1885	6, 7	29, 30	10	227–231	...	4–6	7, 8	223	18	43, 44	51, 52	...	9
86	7, 8	31, 32	11	232–236	...	7–9	9, 10	224	19	45, 46	53, 54	...	10
87	9	33, 34	12	237–242	...	10–12	11, 12	225	20	47, 48	55, 56	1	11
88	10	35, 36	13	243–249	...	13–15	13, 14	226	21	49, 50	57, 58	2, 3	12
89	11	37, 38	14	250–255	...	16–18	15, 16	227	22	(3) 1, 2	59, 60	4, 5	13

* Joining Series 1 and 2 together. Also written as (3) 1, 2, 3, etc.

Year.	Compt. rend.	Dingl. poly. J.	Gazzetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Pharm. Chim.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon. scient.*	Nature.	Phil. Mag.
1860	50, 51	155–158	...	...	...	37, 38	79–81	...	...	...	4	...	19, 20
61	52, 53	159–162	...	...	...	39, 40	82–84	...	...	...	...	...	21, 22
62	54, 55	163–166	...	...	15	41, 42	85–87	...	...	...	...	...	23, 24
63	56, 57	167–170	...	...	16	43, 44	88–90	...	...	..	5	...	25, 26
64	58, 59	171–174	...	...	17	45, 46	91–93	...	...	...	6	...	27, 28
1865	60, 61	175–178	...	...	18	(4) 1, 2	94–96	...	...	...	7	...	29, 30
66	62, 63	179–182	...	...	19	3, 4	97–99	...	...	...	8	...	31, 32
67	64, 65	183–186	...	...	20	5, 6	100–102	...	...	...	9	...	33, 34
68	66, 67	187–190	...	...	21	7, 8	103–105	...	...	...	10	...	35, 36
69	68, 69	191–194	...	...	22	9, 10	106–108	1	...	...	11	1	37, 38
1870	70, 71	195–198	...	...	23	11, 12	(2) 1, 2	2	...	...	12	1, 2, 3	39, 40
71	72, 73	199–202	1	...	24	13, 14	3, 4	3	...	...	13	3, 4, 5	41, 42
72	74, 75	203–206	2	...	25	15, 16	5, 6	4	...	...	14	5, 6, 7	43, 44
73	76, 77	207–210	3	...	26	17, 18	7. 8	5	...	...	15	7, 8, 9	45, 46
74	78, 79	211–214	4	...	27	19, 20	9, 10	6	...	...	16	9, 10, 11	47, 48
1875	80, 81	215–218	5	...	28	21, 22	11, 12	7	...	...	17	11, 12, 13	49, 50
76	82, 83	219–222	6	...	29, 30	23, 24	13. 14	8	...	...	18	13, 14, 15	(5) 1, 2
77	84, 85	223–226	7	...	31, 32	25, 26	15, 16	9	...	...	19	15, 16, 17	3, 4
78	86, 87	227–230	8	...	33, 34	27, 28	17, 18	10	...	...	20	17, 18, 19	5, 6
79	88, 89	231–234	9	1	35, 36	29, 30	19, 20	11	...	...	21	19, 20, 21	7, 8
1880	90, 91	235–238	10	2	37, 38	(5) 1, 2	21, 22	12	...	1	22	21, 22, 23	9, 10
81	92, 93	239–242	11	3	39, 40	3, 4	23, 24	13	...	2	23	23, 24, 25	11, 12
82	94, 95	243–246	12	4	41, 42	5, 6	25, 26	14	1	3	24	25, 26, 27	13, 14
83	96, 97	247–250	13	5	43, 44	7, 8	27, 28	15	2	4	25	27, 28, 29	15, 16
84	98, 99	251–254	14	6	45, 46	9, 10	29, 30	16	3	5	26	29, 30, 31	17, 18
1885	100, 101	255–258	15	7	47, 48	11, 12	31, 32	17	4	6	27	31, 32, 33	19, 20
86	102, 103	259–262	16	8	49, 50	13, 14	33, 34	18	5	7	28	33, 34, 35	21, 22
87	104, 105	263–266	17	9	51, 52	15, 16	35, 36	19	6	8	29, 30	35, 36, 37	23, 24
88	106, 107	267–270	18	10	53, 54	17, 18	37, 38	20	7	9	31, 32	37, 38, 39	25, 26
89	108, 109	271–274	19	11	55, 56	19, 20	39, 40	21	8	10	33, 34	39, 40, 41	27, 28

DropBooks

* See footnote, p. xxii.

Year.	Phil. Trans.	Pogg. Annalen.	Proc. Chem. Soc.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1860	150	109–111	...	10, 11	13	...	39–42	...	...	...	...	...	...
61	151	112–114	...	11	14	...	43, 44	...	...	...	...	...	...
62	152	115–117	...	11. 12	Continued	...	45, 46	...	...	1	...	...	...
63	153	118–120	...	12, 13	as J.	...	47, 48	...	...	2	...	...	...
64	154	121–123	...	13	Chem. Soc.	...	49, 50	...	...	3	...	...	...
1865	155	124–126	...	14	...	...	51, 52	...	...	4	...	...	...
66	156	127–129	...	15	...	...	53, 54	...	...	5	...	...	...
67	157	130–132	...	15, 16	...	...	55, 56	...	...	6	...	...	...
68	158	133–135	...	16, 17	...	...	57, 58	...	...	7	..	...	...
69	159	136–138	...	17, 18	...	...	59, 60	...	...	8	...	...	...
1870	160	139–141	...	18, 19	...	...	61, 62	...	...	9	...	...	...
71	161	142–144	...	19, 20	...	. .	63, 64	...	...	10	...	...	...
72	162	145–147	...	20, 21	...	...	65, 66	...	...	11	...	...	...
73	163	148–150	...	21, 22	...	...	67, 68	...	...	12	...	...	...
74	164	151–153	...	22, 23	...	...	69, 70	...	...	13	...	...	...
1875	165	154–156	...	23, 24	...	...	71, 72	...	...	14	...	...	...
76	166	157–159	...	24, 25	...	...	73, 74	...	...	15	...	...	...
77	167	160	...	25, 26	...	...	75, 76	...	1, 2	16	...	1, 2	...
78	168, 169	Continued	...	27, 28	...	...	77, 78	...	3–5	17	...	2, 3	...
79	170	as Wied. Annalen.	...	28, 29, 30	...	...	79, 80	...	6–8	18	...	3, 4	...
1880	171	...	...	30, 31	...	...	81, 82	...	9–11	19	...	4, 5	...
81	172	...	...	31, 32, 33	...	...	83, 84	1	12–14	20	...	5, 6	...
82	173	...	...	33, 34	...	1	85, 86	2	15–17	21	...	6, 7	...
83	174	...	...	34, 35, 36	...	2	87, 88	3	18–20	22	...	7, 8	...
84	175	...	...	36, 37, 38	...	3	89, 90	4	21–23	23	...	8, 9, 10	...
1885	176	...	1	38, 39	...	4	91, 92	5	24–26	24	...	10, 11	...
86	177	...	2	40, 41	...	5	93, 94	6	27–29	25	...	11, 12	...
87	A. 178	...	3	42, 43	...	6	95, 96	7	30–32	26	...	12, 13	1
88	179	...	4	43, 44, 45	...	7	97	8	33–35	27	1	13, 14, 15	2
89	180	...	5	45, 46, 47	...	8	98	9	36–38	28	2	15	3, 4

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Weekblad.	Chem. Zeit.	Compt. rend.
1890	12	39, 40	15	256–260	19–21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
91	13	41, 42	16	261–266	22–24	19, 20	229	24	5, 6	63, 64	8, 9	...	15	112, 113
92	14	43, 44	17	267–271	25–27	(9) 1, 2	230	25	7, 8	65, 66	10, 11	...	16	114, 115
93	15	45, 46	18	272–277	28–30	3, 4	231	26	9, 10	67, 68	12, 13	...	17	116, 117
94	16	47, 48	19	278–283	(7) 1–3	5, 6	232	27	11, 12	69, 70	14, 15	...	18	118, 119
1895	17	49, 50	20	284–288	4–6	7, 8	233	28	13, 14	71, 72	16, 17	...	19	120, 121
96	18	(4) 1, 2	21	289–293	7–9	9, 10	234	29	15, 16	73, 74	18, 19	...	20	122. 123
97	19	3, 4	22	294–298	10–12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299–303	13–15	13. 14	236	31	19, 20	77, 78	22, 23	...	22	126, 127
99	21, 22	7, 8	24	304–309	16–18	15, 16	237	32	21, 22	79, 80	24, 25	...	23	128, 129
1900	23, 24	9, 10	25	310–313	19–21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
01	25, 26	11, 12	26	314–319	22–24	19, 20	239	34	25, 26	83, 84	28, 29	...	25	132, 133
02	27, 28	13, 14	27	320–325	25–27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	...	26	134, 135
03	29, 30	15, 16	28	326–329	28–30	3, 4	241	36	29, 30	87, 88	32, 33	...	27	136, 137
04	31, 32	17, 18	29	330–337	(8) 1–3	5, 6	242	37	31, 32	89, 90	34, 35	...	28	138, 139
1905	33, 34	19, 20	30	338–343	4–6	7, 8	243	38	33, 34	91, 92	36, 37	...	29	140, 141
06	35, 36	21, 22	31	344–350	7–9	9. 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
07	37, 38	23, 24	32	351–357	10–12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	4	31	144, 145
08	39, 40	25, 26	33	358–363	13–15	13, 14	246	41	3, 4	97, 98	42, 43	5	32	146, 147
09	41, 42	27, 28	34	364–371	16–18	15, 16	247	42	5, 6	99, 100	44, 45	6	33	148, 149
1910	43, 44	29, 30	35	372–377	19–21	17, 18	248	43	7, 8	101, 102	46, 47	7	34	150, 151
11	45, 46	31, 32	36	378–385	22–24	19, 20	249	44	9, 10	103, 104	48, 49	8	35	152, 153
12	47, 48	33, 34	37	386–394	25–27	(11) 1, 2	250	45	11, 12	105, 106	50, 51	9	36	154, 155
13	49, 50	35, 36	38	395–401	28–30	3, 4	251	46	13, 14	107, 108	52, 53	10	37	156, 157
14	Publication	37, 38	39	...	...	5, 6	252	47	15, 16	109, 110	54, 55	11	38	158, 159
1915	ceased	39, 40	40	...	...	...	253	48	17, 18	111, 112	56, 57	12	39	160, 161
16	...	41, 42	41	...	...	...	254	49	19, 20	113, 114	58, 59	13	40	162, 163
17	...	43, 44	42	...	...	...	255	50	21, 22	115, 116	60, 61	14	41	164, 165
18	...	45, 46	43	...	...	...	...	51	23, 24	117	62, 63	15	42	166, 167
19	...	47, 48	44	...	...	...	...	52	25, 26	118, 119	64, 65	16	43	168, 169

DropBooks

Year.	Dingl. poly. J.	Gazzetta.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc.	J. Soc. Chem. Ind.	Monatsh.	Mon.* scient.	Nature.	Phil. Mag.
1890	275–278	20	12	57, 58	...	21, 22	...	41, 42	22	9	11	35, 36	41, 42, 43	29, 30
91	279–282	21	13	59, 60	...	23, 24	...	43, 44	23	10	12	37, 38	43, 44, 45	31, 32
92	283–286	22	14	61, 62	...	25, 26	...	45, 46	24	11	13	39, 40	45, 46, 47	33, 34
93	287–290	23	15	63, 64	...	27, 28	...	47, 48	25	12	14	41, 42	47, 48, 49	35, 36
94	291–294	24	16	65, 66	...	29, 30	...	49, 50	26	13	15	43, 44	49, 50, 51	37, 38
1895	295–298	25	17	67, 68	...	(6) 1, 2	...	51, 52	27	14	16	45, 46	51, 52, 53	39, 40
96	299–302	26	18	69, 70	...	3, 4	...	53, 54	28	15	17	47, 48	53, 54, 55	41, 42
97	303–306	27	19	71, 72	...	5, 6	...	55, 56	29	16	18	49, 50	55, 56, 57	43, 44
98	307–310	28	20	73, 74	...	7, 8	...	57, 58	30	17	19	51, 52	57, 58, 59	45, 46
99	311–314	29	21	75, 76	...	9, 10	...	59, 60	31	18	20	53, 54	59, 60, 61	47, 48
1900	315	30	22	77, 78	...	11, 12	4	61, 62	32	19	21	55, 56	61, 62, 63	49, 50
01	316	31	23	79, 80	...	13, 14	5	63, 64	33	20	22	57	63, 64, 65	(6) 1, 2
02	317	32	24	81, 82	...	15, 16	6	65, 66	34	21	23	58	65, 66, 67	3, 4
03	318	33	25	83, 84	...	17, 18	7	67, 68	35	22	24	59	67, 68, 69	5, 6
04	319	34	26	85, 86	...	19, 20	8	69, 70	36	23	25	60, 61	69, 70, 71	7, 8
1905	320	35	27	87, 88	...	21, 22	9	71, 72	37	24	26	62, 63	71, 72, 73	9, 10
06	321	36	28	89, 90	...	23, 24	10	73, 74	38	25	27	64, 65	73, 74, 75	11, 12
07	322	37	29	91, 92	...	25, 26	11	75, 76	39	26	28	66, 67	75, 76, 77	13, 14
08	323	38	30	93, 94	...	27, 28	12	77, 78	40	27	29	68, 69	77, 78, 79	15, 16
09	324	39	31	95, 96	1	29, 30	13	79, 80	41	28	30	70, 71	79–82	17, 18
1910	325	40	32	97, 98	2	(7) 1, 2	14	81, 82	42	29	31	72, 73	82–85	19, 20
11	326	41	33	99, 100	3	3, 4	15	83, 84	43	30	32	74, 75	85–88	21, 22
12	327	42	34	101, 102	4	5, 6	16	85, 86	44	31	33	76, 77	88, 89, 90	23, 24
13	328	43	35	103, 104	5	7, 8	17	87, 88	45	32	34	78, 79	90, 91, 92	25, 26
14	329	44	36	105, 106	6	9, 10	18	89, 90	46	33	35	80, 81	92, 93, 94	27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
16	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
17	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
18	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100–102	35, 36
19	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102–104	37, 38

* Sec footnote, p. xxii.

Year.	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. anorg. Chem.	Zeitsch. Elektro-Chem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	6	47, 48, 49	9	99	10	39–41	29	3	...	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42–44	30	4	...	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45–47	31	5	1, 2	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48–50	32	6	3, 4, 5	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51–53	33	7	5–7	1	23, 24	13–15
1895	186	...	11	57, 58, 59	14	104	15	54–56	34	8	8–10	1, 2	24, 25	16–18
96	187, 188	...	12	59, 60	15	105	16	57–59	35	9	11, 12, 13	2, 3	26–28	19–21
97	189, 190	...	13	60, 61, 62	16	106	17	60–63	36	10	13–15	3, 4	28, 29	22–24
98	191	...	14	62, 63, 64	17	107	18	64–66	37	11	16–19	4, 5	29–31	25–27
99	192, 193	...	15	64, 65, 66	18	108	19	67–69	38	12	19–22	5, 6	31, 32	28–31
1900	194, 195	1	16	66, 67	19	109	20	Con-	39	13	22–25	6, 7	32–34	32–35
01	196, 197	2	17	68, 69	20	110	21	tinued as	40	14	26–29	7	34–36	36–38
02	198, 199	3	18	69, 70	21	111	22	Annalen	41	15	29–33	8	36, 37	39–42
03	200–202	4	19	71, 72	22	112	23	der	42	16	33–37	9	37–39	43–46
04	203	5	20	72, 73, 74	23	113	24	Physik.	43	17	38–42	10	39, 40	47–49
1905	204, 205	6	21	74–76	24	114	25		44	18	43–48	11	40–42	50–53
06	206	7	22	A. 77, 78	25	115	26		45	19	48–52	12	42, 43	54–57
07	207	8	23	78, 79, 80	26	116	27		46	20	52–56	13	43, 44	58–60
08	207–209	9	24	80, 81	27	117	28		47	21	56–60	14	44–46	61–64
09	209, 210	10	25	82, 83	28	118	29		48	22	61–65	15	46, 47	65–69
1910	210	11	26	83, 84	29	119	30		49	23	65–69	16	48, 49	70–74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	69–73	17	49, 50	75–77
12	211, 212	13	28	86, 87	31	121	32		51	25	73–79	18	50–52	78–80
13	212, 213	14	29	88, 89	32	122	33		52	26	79–83	19	52, 53	81–86
14	213, 214	15	30	89, 90	33	123	34		53	27	84–90	20	54	86–88
1915	215, 216	16	Publication	...	34	...	35		54	28	90–93	21	55	89, 90
16	216, 217	17	of matter	...	35	...	36		55	29	94–98	22	...	91, 92
17	217	18	of scientific	...	36, 37	...	37		56	30	99–101	23	...	92
18	217	...	interest now	...	37	...	38		57	31	102–104	24	No	92
19	...	...	abandoned.	...	38	...	39		58	32	105–109	25	issue*	...

* Remainder of vol. 55 appeared in 1920.

DropBooks

A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOLUME XI. PART I.

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A TEXT-BOOK OF INORGANIC CHEMISTRY.

VOL. XI. PART I.

ORGANOMETALLIC COMPOUNDS.

CHAPTER I.

ORGANOMETALLIC DERIVATIVES OF THE ELEMENTS OF GROUP I.

THE three elements lithium, sodium, and potassium bear little resemblance to copper, silver, and gold in their inorganic derivatives ; but, with the exception of gold, they show more resemblance in their organometallic compounds.

Lithium, sodium, rubidium, and cæsium form two types of compounds, (1) RM, (2) R_2CM, whilst potassium only gives type (2). Lithium and sodium derivatives of type RM are prepared by treating the corresponding mercury alkyls or aryls with the metal in dry benzene or ligroin. Rubidium and cæsium, however, are obtained by interaction of the metal and zinc alkyls. Lithium methyl is best isolated from lithium ethyl and mercury dimethyl in gasoline solution. The most striking property of these metals is their affinity for oxygen, and this property is also exhibited in their organo compounds for they are inflammable in air. The lithium compounds are more crystalline than those of sodium, but the latter are more insoluble in indifferent solvents. It is interesting to note that whilst lithium and its inorganic salts colour the flame red, lithium phenyl burns with a yellow flame.

Schlenk and Marcus in 1914 [1] found that triphenylmethyl chloride reacted with sodium amalgam in dry ether solution, when the operation was carried out in an atmosphere of nitrogen. The resulting compound, sodium triphenylmethyl, was a brick-red mass, decomposed by moisture or carbon dioxide. Kraus and Kawamura in 1923 [2] showed that triphenylmethyl chloride reacts with sodium and potassium in liquid ammonia, but that the potassium compound is more stable than the sodium derivative. A number of compounds similar in structure to triphenylmethyl have since been shown to give similar reactions. Rubidium and cæsium also form similar derivatives.[3]

Copper, silver, and gold are contrasted with the three foregoing

[1] Schlenk and Marcus, *Ber.*, 1914, 47, 1664.
[2] Kraus and Kawamura, *J. Amer. Chem. Soc.*, 1923, 45, 2756.
[3] Grosse, *Ber.*, 1926, 59, 2652.

elements in being stable towards air, water, and some acids, and in these respects bear some analogies to the metals of Group VIII. In organometallic chemistry this likeness is only shared by gold, since this is the only element that forms stable compounds. Copper and silver phenyls have been reported by several investigators, but they are very unstable compounds and little is known about their general behaviour. It will be noted that this instability is shared by the phenyl derivatives of the alkali metals.

Gold [1] forms two tervalent types of compounds, R_2MX and RMX_2, both of which are fairly stable solids. Type R_2MX shows the analogy between gold and thallium, the latter metal giving only this type of organic compound; moreover, no monovalent derivatives of gold or thallium have been isolated. Diethylauric bromide is prepared by the interaction of auric bromide and magnesium ethyl bromide, and this substance is changed to the second type by treating it with bromine in chloroform solution, the halogen replacing one of the ethyl groups. Both compounds precipitate silver bromide from solutions of silver salts, and the diethylauric bromide forms an addition compound with ammonia, when warmed with its aqueous solution. No aryl derivatives of gold have yet been obtained, although when isolated they will be found to be quite stable, and probably have no melting-point below 300° C., like the corresponding thallium compounds.

Lithium.[2]

The lithium alkyls resemble the sodium alkyls in being colourless compounds, but are contrasted to them in being to some extent crystalline. With the exception of the difficultly soluble lithium methyl, they are readily soluble in benzene without decomposition.

Lithium methyl, $LiCH_3$ or LiMe.—When a benzene solution of lithium ethyl and a gasoline solution of mercury dimethyl are mixed, a white microcrystalline powder immediately separates, in accordance with the equation:

$$\underset{\text{soluble}}{2LiEt} + \underset{\text{soluble}}{HgMe_2} = \underset{\text{insoluble}}{2LiMe} + \underset{\text{soluble.}}{HgEt_2}$$

In the dry state the compound is completely colourless, in air it inflames, burning with explosive violence. The flame is red and accompanied by a shower of yellow sparks.

Lithium ethyl, LiC_2H_5, is prepared by the interaction of mercury diethyl and metallic lithium in benzene or ligroin solution. It forms thick, clear, hexagonal plates, melting at 95° C. in a nitrogen atmosphere; at higher temperatures volatilising and condensing in the cooler parts of the apparatus in drops, which soon solidify. It is somewhat soluble in benzene or gasoline, but when exposed to the air the body inflames and burns with the red lithium flame. Lithium ethyl reacts with triethyl-n-butylammonium bromide to give triethylamine and diethyl-n-butylamine, and with tetraethylammonium bromide to give ethane and ethylene.[3]

Lithium n-butyl, LiC_4H_9, with tetraethylammonium bromide

[1] Pope and Gibson, *Trans. Chem. Soc.*, 1907, 91, 2061.
[2] Schlenk and Holtz, *Ber.*, 1917, 50, 262.
[3] Hager and Marvel, *J. Amer. Chem. Soc.*, 1926, 48, 2689.

yields triethylamine; with triethylbenzylammonium bromide it gives diethylbenzylamine; with tri-n-butyl-n-heptylammonium iodide it forms di-n-butyl-n-heptylamine. The following reactions with lithium n-butyl have been carried out,[1] the reacting substance being given first and the products of the reaction shown in brackets: n-heptyl bromide (n-undecane); methylene iodide (n-nonane); β-bromostyrene (phenyl-1-hexene-1, *trans-trans* isomer of diphenyl-1·4-butadiene-1·3 (?)); triphenylchloromethane (triphenylmethyl peroxide, triphenyl-1 : 1 : 1-pentane); o-, m-, p-bromotoluene (toluene).

Lithium iso-amyl,[2] LiC_5H_{11}, reacts with triethyl-n-butylammonium bromide to give diethyl-n-butylamine and lithium n-heptyl, with tetra-n-butylammonium iodide to form tri-n-butylamine, a trace of a hydrocarbon and possibly n-heptane.

Lithium phenyl, $Li.C_6H_5$ or LiPh,[3] may be prepared from mercury diphenyl and metallic lithium or lithium ethyl and mercury diphenyl. In the dry state it is a pure white, microcrystalline powder, which burns in air with a yellow flame, not a red lithium flame.

Lithium triphenylmethyl, $LiCPh_3$,[4] is prepared by treating 1 mol. of triphenylmethyl chloride in anhydrous ether with 6 mols. of lithium in the form of 0·5 per cent. amalgam, in a specially designed flask. It is an orange-red powder and forms a stable etherate, $Li.CPh_3.2Et_2O$. When acted upon by water in the absence of air it decomposes according to the equation:

$$Li.CPh_3 + H_2O = LiOH + CPh_3H$$

Sodium.

The first attempt to obtain sodium alkyls was due to Wanklyn,[5] but his work only led to the formation of sodium-zinc-ethyl double compounds. Schorigin [6] was also unsuccessful in obtaining pure products, whilst Acree [7] described a body which he considered to be sodium phenyl, but this was afterwards refuted by Hilpert and Grüttner.[8]

The sodium alkyls in the pure state are colourless, amorphous, insoluble powders, in indifferent solvents. They decompose when heated to the melting-point. They are extremely inflammable in air, the inflammability decreasing with rising molecular weight of the alkyl residues. Sodium octyl is susceptible to oxygen, large particles igniting in air.[9]

Sodium methyl, $NaCH_3$ or NaMe.—Sodium chips are placed in dry ligroin (B.pt. 80° C.), and all air displaced by dry, oxygen-free nitrogen. The requisite amount of mercury dimethyl is then added and the temperature maintained at 65° C. After several days the product is obtained as a white powder.

Sodium ethyl, NaC_2H_5, is prepared in a similar manner,[10] but the

[1] Marvel, Hager, and Coffman, *J. Amer. Chem. Soc.*, 1927, 49, 2323.
[2] Hager and Marvel, *loc. cit.*
[3] Schlenk and Holtz, *Ber.*, 1917, 50, 262.
[4] Grosse, *Ber.*, 1926, 59, [B], 2652.
[5] Wanklyn, *Annalen*, 1858, 107, 125; 1858, 108, 68; 1859, 111, 234; 1866, 140, 211.
[6] Schorigin, *Ber.*, 1908, 41, 2717; *ibid.*, 1910, 43, 1931.
[7] Acree, *J. Amer. Chem. Soc.*, 1903, 29, 590.
[8] Hilpert and Grüttner, *Ber.*, 1913, 46, 1679.
[9] Schlenk and Holtz, *Ber.*, 1917, 50, 262.
[10] See Schorigin, *Ber.*, 1910, 43, 1931; *ibid.*, 1923, 56, [B], 176.

reaction is complete in one to two hours. **Sodium propyl** and **n-Octyl** have also been obtained.

Sodium phenyl, NaC_6H_5, formed from mercury diphenyl, exhibits the same properties as the alkyls.

Sodium benzyl, $C_6H_5.CH_2.Na$.—Unlike the preceding compounds, sodium benzyl is isolated as an intense red, crystalline powder, insoluble in benzene or ligroin, but fairly soluble in ether, to which it imparts a deep, reddish-yellow colour. The ethereal solution will conduct the electric current, showing that the metallic atom is linked by a carbonium valence. It inflames in air, but if the oxidation is slow, much stilbene is formed. Dry carbon dioxide converts it into sodium phenyl acetate.

Sodium triphenylmethyl, Ph_3CNa.[1]—1. Ten grams of triphenylmethyl chloride in 500 c.c. of dry ether are treated with 200 grams of 2 per cent. sodium amalgam, and the mixture shaken on a machine for one to two hours. During the operations all air must be replaced by nitrogen. A solution of sodium triphenylmethyl is thus obtained in quantitative yield.

2. Ten grams of sodium powder are amalgamated with 10 grams of mercury in 200 c.c. of dry ether, the reaction being carried out in nitrogen. Triphenylmethyl chloride, 2 to 3 grams, is then introduced, the substances melted and put on a shaking machine, the reaction being complete in twelve hours. A dark orange-red solution is obtained; the ether is evaporated and the residue treated several times with petroleum ether and evaporated until a solid is produced. All manipulations are carried out in nitrogen, since air, moisture, or carbon dioxide cause decomposition. The compound forms a brick-red mass.[2]

3. Sodium triphenylmethyl may also be prepared from triphenylmethyl chloride and metallic sodium, when the two are allowed to react in liquid ammonia, and the hydrogen atom of triphenylmethane is replaced by sodium in about an hour.

The compound is very reactive, even at the temperature of liquid ammonia. With water it reacts to form sodium hydroxide and triphenylmethane,

$$Ph_3CNa + H_2O = Ph_3CH + NaOH$$

By the action of oxygen, a white product is formed, the composition of which has not been determined. The reaction with ammonium chloride in liquid ammonia is probably represented by the equations,

$$Ph_3CNa + NH_4Cl = Ph_3CNH_4 + NaCl = Ph_3CH + NH_3 + NaCl$$

The intermediate ammonium compound is not isolated. Ammonium hydroxide with sodium triphenylmethyl yields triphenylmethane and sodamide, and sulphur dioxide forms sodium triphenylmethyl sulphinate.

Sodium triphenylmethyl is moderately soluble in toluene or benzene, but insoluble in petroleum ether and ligroin.

The following are typical reactions of sodium triphenylmethyl with certain organic compounds :—

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[1] Schlenk and Holtz, *Ber.*, 1916, 49, 603; Schlenk and Ochs, *ibid.*, 1916, 49, 608; German Patent 292310; Kraus and Kawamura, *J. Amer. Chem. Soc.*, 1923, 45, 2756.

[2] Schlenk and Marcus, *Ber.*, 1914, 47, 1664.

With triphenylmethyl chloride, hexaphenylethane is produced, the reaction being carried out in liquid ammonia. Thus :

$$Ph_3CNa + Cl.CPh_3 = NaCl + Ph_3C.CPh_3$$

Similarly with dichlorodiphenylmethane, a mixture of hexaphenylethane and pentaphenylethyl is formed.[1] With bromobenzene, using the above solvent, carbon tetraphenyl results,

$$Ph_3CNa + PhBr = NaBr + Ph_4C$$

With methyl benzoate, β-benzpinacolin is formed in accordance with the equation :

$$Ph_3CNa + Ph.CO_2Me = Ph_3C.COPh + NaOMe$$

If methyl p-chlorobenzoate is used, p-chloro-β-benzpinacolin is obtained. Since sodium triphenylmethyl shows a tendency to exchange its sodium atom for hydrogen, it cannot be used for condensations with substances which can function in enolic forms, such as ethyl acetate.

With aldehydes, ethanols are obtained, formaldehyde yielding triphenyl ethanol,

$$Ph_3CNa + OCH_2 = Ph_3C.C(ONa)H_2$$

In the case of benzaldehyde and furfuraldehyde, tetraphenyl ethanol and triphenylfuryl ethanol are isolated respectively.

With ketones as with esters, those which are capable of existing in enolic forms cannot be employed, and diarylketones yield no condensation products, *e.g.* with benzophenone, an ethanol is not formed, but the solution becomes green, since metallic ketyls are produced, according to the equation :

$$Ph_3CNa + COPh_2 \rightleftharpoons Ph_3C.CPh_2.ONa$$

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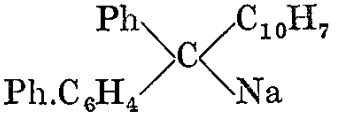
With dibenzalacetone, tetrastyrylpinacolin is formed.

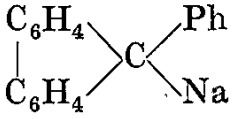
Sodium phenyl-biphenylyl-α-naphthyl-methyl,



Phenyl-biphenylyl naphthyl chloromethane and sodium powder are shaken together for one to two days in dry ether, in the presence of copper bronze. In the solid state it is an indigo-like, metallic, glistening powder, soon becoming dull in air. Its ethereal solution is bluish-violet of extraordinary intensity. With water or ethereal hydrogen chloride the compound is soon decolorised, and when decolorised by air a faint, bright blue-green, air-stable colour remains.

Sodium di-biphenylyl-α-naphthyl-methyl, $(Ph.C_6H_4)_2CNa$, is a black, metallic, glistening powder, immediately becoming yellow-brown in air.

Sodium biphenylene-phenyl-methyl,

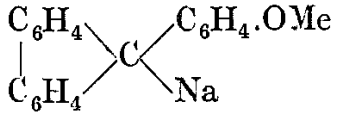


Dibiphenylene-diphenyl-ethane and sodium powder are shaken together

[1] Schlenk and Mark, *Ber.*, 1922, 55, [B], 2285, 2299.

in a nitrogen atmosphere for twelve days. The compound is isolated in shining, orange-red needles, containing one molecule of ether of crystallisation. When dried in a nitrogen atmosphere at 60° C. the ether is removed and the compound darkens, and at higher temperatures it melts to a ruby-red liquid. It is instantly decolorised in air, and warmed with alcohol it dissolves, biphenylene methane crystallising out on cooling.

Sodium p-anisyl-biphenylene-methyl,



is an intensely red, but not distinctly crystalline product, which is obtained free from ether.

Potassium.

No potassium compounds are known of the type RK, only compounds from triphenyl methyl having been obtained.

Potassium triphenylmethyl, $KCPh_3$.[1]—1. Triphenylmethane and metallic potassium are heated at 200° to 220° C. in an indifferent atmosphere. By this method the compound is stated to be red, and when treated with benzyl chloride to yield *as*-tetraphenylethane.

2. Two equivalents of potassium are allowed to react with triphenylmethyl chloride in liquid ammonia.

The compound has a similar appearance and the same properties as the sodium derivative. It exhibits, however, this difference, that whilst sodium triphenyl is unstable in the presence of ammonia, the potassium compound is stable even at 100° C. Moreover, it has not been found possible to synthesise the triphenylmethyl group by the action of triphenylmethyl chloride on potassium triphenylmethyl.

Rubidium.[2]

Rubidium ethyl, RbEt.—The interaction of zinc ethyl and metallic rubidium do not give rubidium ethyl itself, but the double compound with zinc ethyl, $RbEt.ZnEt_2$. This substance crystallises in prisms, which melt in the presence of some zinc ethyl at 70° to 75° C.

Rubidium triphenylmethyl, $RbCPh_3$, prepared in a similar manner to the lithium compound, is a dark-red powder resembling the sodium and potassium derivatives. It gives a blood-red solution in ether.

Cæsium.

Cæsium ethyl, CsEt, is isolated in the same manner as the rubidium compound, but does not seem to be as definite in composition as the latter. It is said to undergo the following reaction :—

$$CsEt + CO_2 = Cs.CO_2.Et$$

The latter compound when treated with sulphuric acid yields propionic acid.

[1] Schlenk and Marcus, *Ber.*, 1914, 47, 1664; Kraus and Kawamura, *J. Amer. Chem. Soc.*, 1923, 45, 2756.

[2] Grosse, *Ber.*, 1926, 59, [B]. 2652.

Cæsium triphenylmethyl, $CsCPh_3$, possesses the same properties as the rubidium compound.

Copper and Silver.

Cuprous phenyl, CuPh.[1]—Cuprous iodide is added to a cold solution of magnesium phenyl bromide in ether. Complete solution takes place, and after a time the cuprous phenyl separates out as a white powder. It decomposes at 80° C. and when warmed with benzene is converted quantitatively into diphenyl and metallic copper, the latter appearing as a mirror. With water, benzene and cuprous oxide are formed, and with dilute nitric acid it is changed to nitrobenzene, concentrated nitric acid causing the compound to explode. Cuprous phenyl blackens in a few days, even when kept in a vacuum.

Magnesium ethyl bromide presumably gives cuprous ethyl, but the compound is unstable above —18° C. and has not been further investigated.

Silver phenyl, AgPh.[2]—Silver bromide is treated with an ethereal solution of magnesium phenyl bromide, the violet solution depositing silver phenyl. The preparation is carried out in absence of light, and the product decomposes in a few hours, even at —18° C., forming silver and diphenyl. The product is highly explosive.

When freshly precipitated silver chloride is used instead of the bromide,[3] a brown, granular powder is obtained. When dry it readily decomposes, evolving clouds of diphenyl fumes. The ratio of silver to phenyl appears to be as 1 : 1. With magnesium p-xylyl- and α-naphthyl bromides and the magnesium compound of p-bromodiphenyl ether, similar compounds are isolated.

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Gold.[4]

Diethylauric bromide, $(C_2H_5)_2AuBr$.—Magnesium ethyl bromide is used in preparing this compound, and it is necessary that it should be free from any unchanged magnesium. Five grams of magnesium are used and the calculated quantity of ethyl bromide in 200 c.c. of anhydrous ether. This Grignard reagent is allowed to drop very slowly into 22 grams of auric bromide in 150 c.c. of dry ether efficiently cooled in ice and salt mixture. Metallic gold begins to appear during the reaction. Powdered ice is carefully added to the mixture and finally water and dilute acetic acid. The liquid is next extracted several times with light petroleum and this is washed with water, then allowed to evaporate in a warm draught cupboard at 25° to 30° C. The residue when once again recrystallised from petroleum ether yields 2 to 3 grams of the pure bromide. No larger yield is obtained if the reaction takes place at the temperature of boiling liquid air, and the yield is less if the auric bromide is added to the Grignard reagent. If auric chloride is used the yield is not increased. Diethylauric bromide takes the form of long, colourless, doubly refracting needles, M.pt. 58° C. It is very soluble in benzene, light petroleum, chloroform, and ether, much less so in alcohol and

[1] Reich, *Compt. rend.*, 1923, 177, 322.
[2] Reich, *ibid.*
[3] Krause and Wendt, *Ber.*, 1923, 56, [B], 2064.
[4] Pope and Gibson, *Trans. Chem. Soc.*, 1907, 91, 2061

insoluble in water. It is volatile at ordinary temperatures and decomposes with explosion at about 70° C. The body is analysed by dissolving it in chloroform, adding bromine in the same solvent, then slowly evaporating to dryness and weighing the residual gold after ignition. Diethylauric bromide is very sensitive to light, in contact with water giving gold. It also gives silver bromide from solutions of silver salts.

Ethylauric dibromide, $C_2H_5AuBr_2$, is prepared by adding a dilute solution of bromine in chloroform to an equimolecular proportion of diethylauric bromide in the same solvent. Crystals of the dibromide are slowly formed. The compound is sparingly soluble in the ordinary organic solvents, but is moderately soluble in warm water. The crystals are transparent, dark, ruby-red, doubly refracting prisms with square ends. On heating it slowly decomposes, but does not melt. It is more stable than the previous body.

Amminodiethylauric bromide, $(C_2H_5)_2AuBrNH_3$, can be obtained from diethylauric bromide on gently warming with dilute aqueous ammonium hydroxide, then evaporating in a vacuum over sulphuric acid. The product is recrystallised from benzene, giving transparent doubly refracting, colourless needles, which decompose on slowly heating at 60° C. The body is soluble in ammonium hydroxide, benzene, acetone, chloroform, or dilute hydrochloric acid. The solution in hydrochloric acid may be boiled without any reduction, and there is no precipitate with platinic chloride, though on long standing metallic gold appears. An aqueous acetone solution of the compound precipitates silver bromide from silver salts.

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CHAPTER II.

ORGANOMETALLIC DERIVATIVES OF THE ELEMENTS OF GROUP II.

THE elements of Group II., along with those of Group V., form more organometallic derivatives than the remaining groups. In so far as Group II. is concerned this is due to the vast number of mercurials now isolated. In 1905, Beckmann [1] found that an ethereal solution of ethyl iodide reacted with metallic calcium to form an etherate, having the constitution $EtCaI.Et_2O$. This was an amorphous powder, fairly stable in air, yielding ethane with water, and was sparingly soluble in ether. Gilman and Schulze [2] repeated Beckmann's work, and came to the conclusion that the compound is not the monoetherate shown above but a di-etherate of calcium iodide, $CaI_2.2Et_2O$. These investigators have also prepared compounds of n-butyl, n-octyl, and phenyl calcium iodides, but in no cases do ether-free compounds appear to have been isolated. They also state that unpublished work on calcium, barium, and strontium dialkyls and diaryls shows that all of these organometallic compounds give positive tests. Since the purpose of this chapter is to deal with pure compounds and not molecular complexes, no further account is given of the calcium compounds.[3]

The remaining members of this group form a series of organo compounds in which the stability increases with rising atomic weight from beryllium to mercury. It should be pointed out that the authors do not include the Grignard compounds under magnesium, since these are not actually isolated in reactions in which they are employed. Moreover, the so-called " individual " magnesium alkyl salts, which do not contain combined ether, have not been used to any great extent for synthetic purposes.

The dimethyl compounds of the metals from beryllium to cadmium are all very volatile liquids, the beryllium, magnesium, and zinc derivatives exploding when treated with water, the cadmium decomposing slowly under the same conditions.

Beryllium compounds were obtained in 1860 by Cahours [4] by heating metallic beryllium with mercury dialkyls at 130° to 135° C. in a sealed tube. Frankland [5] also obtained beryllium diethyl and dipropyl by a similar method. In 1884, Lavroff [6] also claimed to have obtained

[1] Beckmann, *Ber.*, 1905, 38, 904.
[2] Gilman and Schulze, *J. Amer. Chem. Soc.*, 1926, 48, 2463.
[3] See Dufford, Nightingale, and Calvert, *J. Amer. Chem. Soc.*, 1925, 47, 95; Gilman and Pickens, *ibid.*, 1925, 47, 2406; Gilman and Schulze, *ibid.*, 1925, 47, 2002.
[4] Cahours, *Annalen*, 1860, 114, 243; *Jahresber.*, 1873, p. 520.
[5] Frankland, *Trans. Chem. Soc.*, 1861, 13, 181, 194.
[6] Lavroff, *J. Russ. Phys. Chem. Soc.*, 1884, 16, 93; *Bull. Soc. chim.*, 1884, 41, 548.

beryllium dimethyl. No further reference is made to the compounds until 1923, when Krause and Wendt [1] stated that beryllium dialkyls may be prepared by the interaction of beryllium chloride and an excess of Grignard reagent.

The actual isolation of beryllium dialkyls in a pure state has only just been accomplished by Gilman and Schulze,[2] and their work throws doubt upon the accuracy of that of previous investigators. Their method of procedure is the one suggested by Krause and Wendt. In 1926, Durand [3] claimed to have prepared beryllium methyl iodide, but the work has since been disproved by Gilman and Schulze.[4] These workers have isolated beryllium alkyl halides by heating beryllium, alkyl halides, and ether in the presence of catalysts, such as mercuric chloride, beryllium chloride, or free bromine. The first aryl compound, beryllium phenyl iodide, has been prepared by a similar process.

The first attempt to prepare organic compounds of magnesium was due to Hallwachs and Schafarik [5] in 1859, these investigators heating metallic magnesium with ethyl iodide in a sealed tube at 150° to 180° C. Upon opening the tube a gas was evolved and a white mass obtained. This when heated gave a colourless liquid of penetrating odour, which did not inflame. In view of later work the products appear to be magnesium iodide and traces of magnesium diethyl. A year later, Cahours [6] repeated the above work, the reacting substances being heated for several hours at 130° C. He isolated magnesium iodide and a colourless, strongly volatile liquid, inflaming in air, and having a leek-like odour. This liquid Cahours mistook for magnesium diethyl. In 1891, Löhr [7] obtained magnesium dialkyls by heating magnesium with mercury dialkyls, and later Fleck [8] extended Löhr's work. No further work was done on these substances until 1927, when Gilman and Schulze [9] used Löhr's method, but introduced mercuric chloride into the reaction as a catalyst. This work proves that the substances obtained by the earlier investigators were not very pure.

Only one aryl compound is known, namely, magnesium diphenyl,[10] formed by heating magnesium powder and mercury diphenyl at 200° C. in an atmosphere of nitrogen. Like the alkyl compounds, it is readily oxidisable in air and decomposed by water.

Frankland in 1853 [11] obtained the first zinc alkyl, zinc dimethyl, by heating methyl iodide with an excess of zinc in a sealed tube at 150° to 160° C. From this beginning, the series was gradually continued as far as zinc di-isoamyl, in the hands of various investigators. The lower members are spontaneously inflammable in air, this property decreasing as the series is ascended, and all the compounds are decomposed by water, the lower ones with violent explosion. These compounds have proved of great value in many organic syntheses, but their use has been eliminated to a large extent by the Grignard reagent owing to the fact

[1] Krause and Wendt, *Ber.*, 1923, 56, 467.
[2] Gilman and Schulze, *J. Chem. Soc.*, 1927, p. 2663.
[3] Durand, *Compt. rend.*, 1926, 182, 1162.
[4] Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, 49, 2904.
[5] Hallwachs and Schafarik, *Annalen*, 1859, 109, 206.
[6] Cahours, *Annalen*, 1860, 114, 240.
[7] Löhr, *Annalen*, 1891, 261, 48.
[8] Fleck, *Annalen*, 1893, 276, 129.
[9] Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, 49, 2328.
[10] Hilpert and Grüttner, *Ber.*, 1913, 46, 1675.
[11] Frankland, *Annalen*, 1853, 85, 347.

that the latter need not be isolated in reactions in which it is used, whereas the inflammability of the zinc alkyls renders them difficult to handle. Zinc alkyls have also been used in the preparation of organometallic derivatives of mercury,[1] boron,[2] aluminium,[3] thallium,[4] silicon,[5] germanium,[6] tin,[7] lead,[8] phosphorus,[9] arsenic,[10] antimony,[11] bismuth.[12]

No zinc aryls were known until 1913, when Hilpert and Grüttner [13] isolated zinc diphenyl by boiling mercury diphenyl with zinc for two minutes in an atmosphere of hydrogen. The rapidity with which this reaction takes place resembles the preparation of aluminium triphenyl from mercury diphenyl and aluminium, the reaction being complete in ten to fifteen seconds at 140° C. The zinc diphenyl is affected by light, and, like magnesium diphenyl, is oxidised by atmospheric oxygen and decomposed by water. An interesting use has recently been made by Chambers and Scherer [14] of zinc diphenyl. In order to prepare tin tetraphenyl, magnesium phenyl bromide is treated with anhydrous zinc chloride in ethereal solution, the ether replaced by toluene and the product treated with stannic chloride. Thus the zinc compound is merely used as an intermediate without being isolated, in the same way as the Grignard reagent.

Although cadmium alkyls were known as early as 1853,[15] it was not until 1917 [16] that they were obtained in good yield in a state of purity. The general method of preparation is by the interaction of magnesium alkyl halides and cadmium halides. In common with the other alkyls so far described in this chapter they are very volatile, the methyl derivative even being difficult to separate from ether, since it volatilises along with the vapour of the latter. This volatility decreases as the series is ascended from methyl to isoamyl, and although the higher compounds are

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[1] Buckton, *Annalen*, 1859, 109, 219, 221; *Jahresber.*, 1858, p. 390; Frankland, *Annalen*, 1859, 111, 57; *Jahresber.*, 1859, p. 413; Krassowski, *Zeitschrift für Chemie*, 1870, p. 528; *Ber.*, 1870, 3, 625; Oppenheim, *Ber.*, 1871, 4, 671.

[2] Frankland, *Annalen*, 1862, 122, 132, 144; *Jahresber.*, 1876, p. 469.

[3] Buckton and Odling, *Annalen Spl.*, 1861, 4, 110, 112; Cahours, *Annalen*, 1860, 114, 242; Hallwachs and Schafarik, *Annalen*, 1859, 109, 207; Fürstenhoff, *Chem. Zentr.*, 1904, 1. 785; Buckton and Odling, *Proc. Roy. Soc.*, 1865, 14, 19; Cahours, *Jahresber.*, 1873, p. 518; *Ber.*, 1873, 6, 567; *Compt. rend.*, 1873, 76, 133, 748, 1383.

[4] Hartwig, *Ber.*, 1874, 7, 298; *Annalen*, 1875, 176, 264.

[5] Friedel and Crafts, *Annalen*, 1865, 136, 203; 1863, 127, 31; Ladenburg, *Annalen*, 1872, 164, 302, 327; Pape, *Annalen*, 1884, 222, 359, 370; Ladenburg, *Annalen*, 1874, 173, 148; Friedel and Ladenburg, *Ann. Chim. Phys.*, 1880, [5], 19, 401; *Annalen*, 1880, 203, 251.

[6] Winkler, *J. prakt. Chem.*, 1845, [2], 36, 204.

[7] Cahours, *Annalen*, 1862, 122, 59; *Jahresber.*, 1873, p. 519; Frankland, *Annalen*, 1859, 111, 50; Frankland and Lawrance, *Trans. Chem. Soc.*, 1879, 35, 130; Morgunow, *Annalen*, 1867, 144, 157; Buckton, *Annalen*, 1859, 109, 225; Pope and Peachey, *Proc. Chem. Soc.*, 1912, 28, 42, 116.

[8] Cahours, *Annalen*, 1862, 122, 67; Buckton, *Annalen*, 1859, 109, 222; 1859, 112, 226; Frankland and Lawrance, *J. Chem. Soc.*, 1879, 35, 245.

[9] Cahours and Hofmann, *Annalen*, 1857, 104. 1; Hofmann, *Annalen Spl.*, 1861, 1, 7; Drechsel and Finkelsteln, *Ber.*, 1871, 4, 352; Wichelhaus, *Ber.*, 1868, 1, 80.

[10] Cahours and Hofmann, *Compt. rend.*, 1855, 41, 834; *Jahresber.*, 1855, p. 538; Cahours, *Annalen*, 1862, 122, 219; Hofmann, *Annalen*, 1857, 103, 357.

[11] Buckton, *Trans. Chem. Soc.*, 1863, 16, 22; *Jahresber.*, 1863, p. 470.

[12] Marquardt, *Ber.*, 1887, 20, 1517; *ibid.*, 1888, 21, 2038.

[13] Hilpert and Grüttner, *Ber.*, 1913, 46, 1675.

[14] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, 48, 1054.

[15] Löhr, *Annalen*, 1853, 87, 55.

[16] Krause, *Ber.*, 1917, 50, 1813.

decomposed by water, the process takes some hours to reach completion. As in the case of magnesium and zinc, only one aryl compound of cadmium is known, cadmium diphenyl. It is prepared by heating mercury diphenyl and metallic cadmium in an atmosphere of hydrogen, but the product appears to be very unstable in the dry state, discolouring in a vacuum desiccator even when allowed to stand for an hour.[1] The cadmium may be replaced by mercury or zinc under suitable conditions.

The only remaining metal in the group to be discussed is mercury. This element forms such an enormous variety of organic compounds that they are dealt with in subsequent chapters. No other element is known which will replace the hydrogen of organic derivatives with such ease. All other metals of the periodic classification are only introduced singly into organic residues, whereas two to five mercury residues may become attached to a molecule in a single operation, *e.g.* penta-acetoxy-mercuriacetanilide. Like the other members of Group II., it forms compounds of the type R_2M, but these are far more stable than any previously described. A second type, RMX, is also known, which resembles the Grignard reagent RMgX in formula only, showing no other relation to the magnesium compounds. These two types of mercury compounds are dealt with in the subsequent chapter.

Beryllium.

Beryllium dimethyl, $Be(CH_3)_2$.[2]—This compound is prepared by the interaction of anhydrous beryllium chloride and magnesium methyl iodide. Owing to the hygroscopic nature of the beryllium chloride and the instability of beryllium dimethyl in air, the reaction is carried out in a specially designed apparatus in an atmosphere of dry hydrogen or nitrogen. Beryllium dimethyl crystallises from hot concentrated ethereal solution in snow-white needles, and it has the same form when it sublimes at about 200° C. without melting. Its ethereal solutions fume strongly on exposure to the atmosphere. When suddenly overheated, it is partially decomposed, leaving a brown or grey mirror. In air it is spontaneously inflammable, especially in the presence of moisture, burning with a luminous flame, and evolving white fumes of beryllium oxide. It is violently decomposed by water, yielding methane. In the solid state it even inflames when treated with carbon dioxide, but if in ethereal solution it yields acetic acid. It reacts with phenyl carbimide in ethereal solution giving the anilide, and with α-naphthyl carbimide, aceto-α-naphthalide is formed. With Michler's ketone it gives an immediate positive colour reaction, with benzophenone it forms diphenylmethylcarbinol, and with benzoyl chloride phenyldimethylcarbinol is produced. The reaction with iodine is very vigorous, probably forming beryllium methyl iodide.

Beryllium diethyl, $Be(C_2H_5)_2$, prepared in a similar manner to the preceding compound, is a colourless liquid, B.pt. 93° to 95° C. at 4 mm. or 110° C. at 15 mm. It distils at 180° to 240° C. at ordinary pressure, with considerable decomposition, and when solidified in carbon dioxide-ether freezing mixture white crystals are formed, which melt on warming to −13° to −11° C. It resembles the corresponding dimethyl derivative in oxidisability and inflammability. With water it yields

[1] Hilpert and Gruttner, *Ber.*, 1913, 46, 1675.
[2] Gilman and Schulze, *J. Chem. Soc.*, 1927, p. 2663.

ethane, and its ethereal solution with carbon dioxide gives triethylcarbinol. It gives a positive colour reaction with Michler's ketone, reduces benzophenone to benzhydrol, reacts vigorously with iodine and with an excess of an ethereal solution of beryllium chloride, a solution having the characteristics of beryllium ethyl chloride is obtained.[1]

Beryllium propyl, $Be(C_3H_7)_2$, is a liquid, B.pt. 244° to 246° C., and does not solidify at −17° C.

Beryllium di-n-butyl,[2] $Be(C_4H_9)_2$, is a clear, colourless liquid, having a mercaptan-like odour. It boils at 170° C. at 25 mm. It oxidises rapidly in air, but is not spontaneously inflammable. It is decomposed by water, reacts with phenylcarbimide, and gives a blue colour with Michler's ketone.

Beryllium diphenyl, $Be(C_6H_5)_2$, and **beryllium di-p-tolyl,** $Be(C_6H_4.CH_3)_2$, may be readily prepared by heating beryllium with equivalent quantities of mercury diphenyl and mercury di-p-tolyl and a trace of mercuric chloride in sealed tubes at 225° C. for six hours.

Beryllium methyl and ethyl iodides,[3] $Be(CH_3)I$ and $Be(C_2H_5)I$. —These compounds are best prepared as follows: About 0·5 gram of powdered beryllium, 0·2 to 0·5 gram of mercuric chloride, 5 c.c. of the alkyl halide, and 25 c.c. of ether are heated for at least fifteen hours at 80° to 90° C. in a suitable bottle, the neck of which has been drawn out to a fine capillary. The product is then removed from the bottle by breaking the capillary, the pressure inside being sufficient to force the liquid out.

The ethereal solutions of these iodides do not fume in air, and removal of the solvent gives a liquid, which on further heating evolves dense white fumes, probably of beryllium oxide. Heating changes the alkyl beryllium halides to beryllium dialkyls. All the alkyl halide compounds are decomposed by water, with formation of the corresponding hydrocarbon. When carbon dioxide is passed through ethereal beryllium methyl iodide for three hours, the solution still gives a positive test and no acetic acid is found after hydrolysis. Acetanilide is formed from beryllium methyl iodide and phenyl isocyanate.

In a similar manner *beryllium ethyl bromide,* $Be(C_2H_5)Br$, and *beryllium n-butyl iodide,* $Be(C_4H_9)I$, are prepared. In these cases beryllium chloride or free bromine may be used as catalysts.

Beryllium phenyl iodide, $Be(C_6H_5)I$, gives a positive test when prepared in the presence of mercuric chloride after fifteen hours heating at 80° to 90° C., and is also readily prepared by heating at 150° to 175° C. with either mercuric or beryllium chloride as catalyst.

Magnesium.

Magnesium dimethyl, $Mg(CH_3)_2$,[4] may be prepared by heating magnesium turnings with mercury dimethyl for thirty-six hours at 130° C. It is described as a grey-yellow mass, which reacts with explosive violence with water. The addition of acetyl chloride to a well-cooled ethereal solution of the compound in a nitrogen atmosphere

[1] Cahours, *Annalen,* 1860, 114, 243.
[2] Gilman and Schulze, *loc. cit.*
[3] Gilman and Schulze, *J. Amer. Chem. Soc.,* 1927, 49, 2904; see Durand, *Compt. rend.,* 1926, 182, 1162.
[4] Löhr, *Annalen,* 1891, 261, 48; Fleck, *Annalen,* 1893, 276, 129.

yields trimethyl carbinol. When hydrogen iodide is passed into the mixture, tertiary butyl iodide is formed.

Magnesium diethyl, $Mg(C_2H_5)_2$.[1]—Fresh mercury diethyl and magnesium powder are heated together in a sealed tube at 130° C. in the presence of a small amount of mercuric chloride. The product thus isolated is a light grey or brown powder, spontaneously inflammable in air. Magnesium diethyl is soluble in ether, this solution reacting with an ethereal solution of acetyl chloride to give methyldiethyl carbinol.

Magnesium dipropyl, $Mg(C_3H_7)_2$, has been prepared without the use of a catalyst.[2]

Magnesium diphenyl, $MgPh_2$.—Mercury diphenyl and magnesium powder are heated to 200° C. in an atmosphere of nitrogen, when the magnesium compound is isolated as a white powder. It is insoluble in carbon disulphide or benzene, but soluble in absolute ether, and when boiled in the latter solvent in a stream of hydrogen, filtered and evaporated under 5° C. the compound crystallises in transparent feathery needles. These contain ether of crystallisation which may be removed by the heat of the hand, an amorphous product resulting.[3] It burns in air, forming magnesium oxide, and by slow oxidation gives $Mg(OPh)_2$. Water decomposes magnesium diphenyl with the formation of benzene and magnesium hydroxide. Bromine in ethereal solution forms bromobenzene and magnesium bromide, no magnesium phenyl bromide being isolated. With phosphorus trichloride only traces of diphenyl phosphorus chloride are formed. Benzal chloride reacts with the compound when heated for three hours in a sealed tube at 100° C., giving triphenyl methane and magnesium chloride. When magnesium diphenyl is heated in a sealed tube at 280° C. until it decomposes, the principal product obtained by extraction of the product with benzene is diphenyl.

Zinc.

Zinc dimethyl, $Zn(CH_3)_2$ or $ZnMe_2$, may be prepared in several ways :

1. By heating methyl iodide with an excess of zinc in a sealed tube at 150° to 160° C.[4]

2. Methyl iodide and dry zinc turnings or dust are heated for six to nine days in an iron flask carrying a reflux condenser, the reaction product being distilled in an atmosphere of carbon dioxide.[5]

3. Methyl iodide and zinc are heated together to form zinc methyl iodide, Me.ZnI, which is decomposed on distillation to yield zinc methyl and zinc iodide.[6]

4. Three parts of methyl iodide and two parts of anhydrous ether

[1] Gilman and Schulze, *J. Amer. Chem. Soc.*, 1927, 49, 2328 ; see Löhr, *ibid.* ; Fleck, *ibid.*

[2] Fleck, *loc. cit.*

[3] Hilpert and Grüttner, *Ber.*, 1913, 46, 1675 ; Waga, *Annalen*, 1894, 281, 320.

[4] Frankland, *Annalen*, 1853, 85, 347 ; see also Butlerow, *Annalen*, 1867, 144, 2.

[5] Ssimonowitsch, *J. Russ. Phys. Chem. Soc.*, 1898, 30, 40 ; *Chem. Zentr.*, 1899, i. 1066 ; see Worobjeff, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 45 ; *Chem. Zentr.* 1899, i. 1067 ; Ipatiew, *J. prakt. Chem.*, 1896, [2], 53, 275 ; Kaulfuss, *Ber.*, 1887, 20, 3104.

[6] Frankland, *Annalen*, 1855, 95, 28 ; Wanklyn, *Trans. Chem. Soc.*, 1861, 13, 124 ; Fileti and Cantapulo, *Gazzetta*, 1892, 22, ii. 388 ; Lachmann, *Amer. Chem. J.*, 1900, 24, 33, 34.

are heated with zinc in a copper digester at 100° C. for six hours. The reaction mixture is then distilled from the water-bath, the fraction between 48° to 51° C. corresponding to $2ZnMe_2.Et_2O$. If methyl ether is used, $2ZnMe_2.Me_2O$ is obtained, which distils about 43° C., and in the absence of ether, pure zinc dimethyl is isolated.[1]

5. One hundred and twenty parts of methyl iodide, 90 parts of zinc, and 100 parts of 1 per cent. sodium amalgam and a drop of ethyl acetate are mixed in the cold. They are then heated to 45° C. for thirty-six hours and the bath finally raised to 90° C., when the contents of the flask solidify. Distillation from an oil bath produces zinc dimethyl, distilling at 47° C. constant.[2]

6. By heating methyl iodide with zinc-copper couple.[3]

Zinc dimethyl is a colourless, strongly refracting liquid, having a characteristic, pungent smell and is very volatile. When cooled in a freezing mixture it solidifies and melts at −40° C.[4] It boils at 46° C. and has a density of 1·386 at 10·5° C.[5] In air it is spontaneously inflammable, burning with a greenish-blue flame,[6] but if the oxidation is allowed to proceed slowly, zinc methyl methylate, ZnMe.OMe, is produced, together with some zinc methylate, $Zn(OMe)_2$.[7] Water decomposes zinc dimethyl with formation of zinc hydroxide and methane. Zinc dimethyl undergoes reactions with various substances, as indicated in the following table :—

REACTIONS OF ZINC DIMETHYL.

Reacting Substance.	Resulting Products.	References.
Sulphur dioxide.	Methane sulphinic acid.	Hobson, *Annalen*, 1858, 106, 288.
Nitric oxide.	Compound of methylnitroso-hydroxylamine. $ZnMe_2.Zn(CH_3O_2N_2)_2$.	Frankland, *Annalen*, 1856, 99, 369.
Phosgene.	Trimethylcarbinol.	Butlerow, *Jahresber.*, 1863, p. 475; 1864, p. 496.
Tertiary butyl iodide.	Tetramethylmethane.	Lwow, *Zeitsch. Chem.*, 1870, p. 520.
Acetone Chloride, Me_2CCl_2.	Tetramethylmethane.	Lwow, *Zeitsch. Chem.*, 1871, p. 257.
Acetyl chloride, then water.	Acetone.	Freund, *Annalen*, 1861, 118, 12; Butlerow, *Annalen*, 1867, 144, 2; see Pawlow, *Annalen*, 1877, 188, 106, 114, 118.
Acetyl chloride, using excess of zinc dimethyl, then treating with water after long standing.	Trimethylcarbinol.	

[1] Frankland, *Trans. Chem. Soc.*, 1861, 13, 124; see also Wanklyn, *loc. cit.*
[2] Ladenburg, *Annalen*, 1874, 173, 147; Wagner, *J. prakt. Chem.*, 1891, [2], 44, 261.
[3] Renshaw and Greenlaw, *J. Amer. Chem. Soc.*, 1920, 42, 1472.
[4] Hasse, *Ber.*, 1893, 26, 1053.
[5] Frankland and Duppa, *Annalen*, 1864, 130, 119.
[6] Frankland, *Annalen*, 1853, 85, 347.
[7] Butlerow, *Zeitsch. Chem.*, 1864, p. 403; *Jahresber.*, 1864, p. 467.

Reactions of Zinc Dimethyl—*continued.*

Reacting Substance.	Resulting Products.	References.
Chloral.	Trichloroisopropyl alcohol.	Garzarolli-Thurnlakh, *Annalen*, 1881, 210, 77.
Silicon tetrachloride.	Silicon tetramethyl.	Friedel and Crafts, *Ann. Chim. Phys.*, 1870, [4], 19, 360; *Annalen*, 1865, 136, 203.
Lead chloride.	Lead tetramethyl.	Cahours, *Annalen*, 1862, 122, 67.
Phosphorus trichloride.	Compound of zinc chloride and trimethyl phosphine.	Cahours and Hofmann, *Compt. rend.*, 1855, 41, 832; *Jahresber.*, 1885, p. 537; *Annalen*, 1857, 104, 29.
Arsenic trichloride.	Trimethylarsine.	do.
Tin diethyl di-iodide.	Tin dimethyl diethyl.	Frankland, *Annalen*, 1859, 111, 50.
Tin triethyl iodide.	Tin methyl triethyl.	Cahours, *Annalen*, 1862, 122, 60.
Methylmercuric iodide.	Mercury dimethyl.	Buckton, *Annalen*, 1859, 109, 222.
Methyl alcohol (small quantity).	Zinc methyl methylate.	Butlerow, *Jahresber.*, 1864, p. 467.
,, (excess).	Zinc methylate.	do.
Ethyl alcohol.	Zinc ethylate.	Tolkatschew, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 470; *Chem. Zentr.*, 1901, ii. 1200.
Acetone.	Mesityl oxide and higher condensation products.	Pawlow, *Annalen*, 1877, 188, 133.
Chloroformic ethyl ester.	Ethylene, methane, carbon dioxide, zinc chloride.	Butlerow, *Jahresber.*, 1863, p. 474; *Zeitsch. Chem.*, 1863, p. 486.
1-Bromo-1-nitroethane.	2-Nitropropane.	Bewad, *J. prakt. Chem.*, 1893, [2], 48, 352.
Tetraethylester of orthosilicic acid.	Zinc methyl ethylate, triethyl ester of methyl orthosilicic acid.	Ladenburg, *Annalen*, 1874, 173, 148.

Zinc diethyl, $Zn(C_2H_5)_2$ or $ZnEt_2$, may be obtained:

1. Ninety grams of zinc filings and 10 grams of finely divided copper (from the oxide) are heated with a good flame in a 300-c.c. capacity flask, to form a couple. Then 87 grams of ethyl iodide are added and the whole heated at 90° C. In fifteen minutes the conversion to ethiodide is complete and the product is distilled in a hydrogen atmosphere, 31 grams of zinc diethyl being obtained, 90·4 per cent.[1]

[1] Gladstone and Tribe, *Trans. Chem. Soc.*, 1879, 35, 571; see Lachman, *Amer. Chem. J.*, 1900, 24, 32.

2. By heating ethyl iodide with an excess of zinc in a sealed tube at 150° to 160° C.[1]

3. Equal volumes of ether and ethyl iodide are heated in a copper digester at 130° C. and the reaction product distilled.[2]

4. By heating an alloy of zinc and sodium with ethyl iodide in a carbon dioxide atmosphere.[3]

5. Mercury diethyl and zinc are heated in a sealed tube at 100° C.[4]

Zinc diethyl is a colourless liquid of penetrating odour, spontaneously inflammable in air.[5] It may be solidified in a freezing mixture and melts at −28° C.[6] It boils at 118° C., and has a density of 1·182 at 18° C. and 1·245 at 8° C.[7]

The molecular refraction and dispersion of zinc diethyl compared with tin tetraethyl is as follows :—[8]

	Temp.	Density.	n_A.	n_D.	n_F.	n_H.
$ZnEt_2$	8·0° C.	1·245	1·4936	..	1·5141	1·5336
$SnEt_4$	0° C.	1·4089	1·5065	1·5143	..	1·5403

Experimental.		Theoretical.	
Molecular Refraction.	Molecular Dispersion.	Molecular Refraction.	Molecular Dispersion.
$ZnEt_2$ 48·88	3·97	42 8	..
$SnEt_4$ 48·12	5·54	84·6	..

DropBooks

The heat of formation of zinc diethyl from its elements is as follows :—[9]

$$[Zn]+4[C]+5(H_2)=ZnEt_2-31{,}800 \text{ calories.}$$

Zinc diethyl is decomposed by sulphuric and hydrochloric acids with evolution of heat :

$$ZnEt_2+H_2SO_4=2C_2H_6+ZnSO_4+79{,}800 \text{ calories.}$$
$$ZnEt_2+2HCl=2C_2H_6+ZnCl_2+78{,}000 \text{ calories.}$$

[1] Frankland, *Annalen*, 1853, 85, 360.

[2] Frankland, *Annalen*, 1855, 95, 28 ; see also Pebal, *Annalen*, 1861, 118, 22 ; *ibid.*, 1862, 122, 105.

[3] Rieth and Beilstein, *Annalen*, 1862, 123, 246 ; 1863, 126, 248 ; see also Alexeyeff and Beilstein, *Jahresber.*, 1864, p. 469 ; *Compt. rend.*, 1864, 58, 171 ; Bewad, *J. prakt. Chem.*, 1849, [2], 48, 350 ; Rathke, *Annalen*, 1869, 152, 220.

[4] Frankland and Duppa, *Trans. Chem. Soc.*, 1864, 17, 29 ; *Annalen*, 1864, 130, 117. For other methods using zinc and ethyl iodide, see Frankland, *Annalen*, 1853, 85, 360 ; Wichelhaus, *Annalen*, 1869, 152, 321 ; Ssimonowitsch, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 40 ; *Chem. Zentr.*, 1899, i. 1066 ; Fileti and Cantapulo, *Gazzetta*, 1892, 22, ii. 387 ; Chapman, *Zeitschrift für Chemie*, 1867, p. 74; Kahlfuss, *Ber.*, 1887, 20, 3154; Schon, *J. prakt. Chem.*, 1850, [2], 51, 100.

[5] Frankland, *Annalen*, 1855, 95, 42.

[6] Haase, *Ber.*, 1893, 26. 1053.

[7] Gladstone, *Trans. Chem. Soc.*, 1891, 59, 293.

[8] Gladstone, *ibid.*

[9] Guntz, *Jahresber.*, 1887, p. 242.

The reactions between zinc diethyl and various compounds have been collected together in the following table :—

REACTIONS OF ZINC DIETHYL.

Reacting Substance.	Resulting Products.	References.
Chlorine, bromine, or iodine.	Decomposition with violence, inflaming in the case of chlorine.	Frankland, *Annalen.* 1855, 95, 51.
Bromine or iodine in ether solution.	Ethyl halide, zinc halide.	do.
Air passed through ether solution of zinc diethyl.	Compound EtZn.O.O.Et.	Demuth and Meyer, *Ber.*, 1890, 23, 394 ; see also Frankland, *Annalen*, 1855, 95, 42 ; Frankland and Duppa, *Annalen*, 1865, 135, 30.
Water.	Zinc hydroxide, ethane.	Frankland, *Annalen*, 1853, 85. 360.
Sulphur dioxide or trioxide.	Ethane sulphinic acid.	Wischin, *Annalen*, 1866. 139. 367 ; see also Hobson, *Annalen*, 1857. 102, 76.
Nitric oxide.	Compound $ZnEt_2.Zn(C_2H_5O_2N_2)_2$.	Frankland, *Annalen*, 1856, 99, 345.
Ammonia gas passed into ether solution of zinc diethyl.	Zincamide. $Zn(NH_2)_2$.	Frankland, *Jahresber.*, 1857. p. 418 ; *J. prakt. Chem.*, 1858, [1], 73, 35.
Cyanogen.	Ethyl cyanide.	Frankland and Graham, *Trans. Chem. Soc.*, 1880, 37, 740.
Cyanogen chloride.	Ethyl cyanide.	Gal, *Compt. rend.*, 1868, 66, 49 ; *Annalen*, 1868, 147, 27.
Cyanogen iodide.	Zinc cyanide, ethyl iodide.	Calmels, *Compt. rend.*, 1884, 99, 239 ; *Bull. Soc. chim.*, 1885, [2], 43, 82.
Liquid carbon dioxide under pressure.	Zinc propionate.	Schmitt, *J. prakt. Chem.*, 1847, [2], 42, 568.
Sodium.	Compound $ZnEt_2.NaEt$.	Wanklyn, *Annalen*, 1858, 107. 125 ; 1858, 108, 70.
Phosphorus trichloride.	Compound of zinc chloride and triethylphosphine.	Cahours and Hofmann, *Compt. rend.*, 1855, 41, 832 ; *Jahresber.*, 1855, p. 537 ; *Annalen*, 1857, 104, 7 ; *Annalen Spl.*, 1861, 1, 2.
Arsenic trichloride.	Triethylarsine.	do.
Antimony trichloride.	Triethylstibine.	Hofmann, *Annalen*, 1857, 103, 357.
Silicon tetrachloride.	Silicon tetraethyl.	Friedel and Crafts, *Ann. Chim. Phys.*, 1870, [4], 19, 335 ; *Annalen*, 1863, 127, 31.

Reactions of Zinc Diethyl—*continued.*

Reacting Substance.	Resulting Products.	References.
Stannous chloride.	Tin tetraethyl.	Frankland and Lawrance, *Trans. Chem. Soc.*, 1879, 35, 130.
Lead chloride.	Lead tetraethyl.	Buckton, *Annalen*, 1859, 109. 223; 112, 226: Frankland and Lawrance, *Trans. Chem. Soc.*, 1879, 35, 244.
Mercurous or mercuric chloride.	Mercury diethyl.	Buckton, *Annalen*, 1859, 109, 219; *Jahresber.*, 1858, p. 390.
Cupric chloride.	Ethane, butane, ethylene, metallic copper.	Wanklyn and Carius, *Annalen*, 1861, 120, 69.
Silver chloride, ferric iodide, zirconium chloride, titanium chloride.	Similar to above.	Wanklyn and Carius, *ibid.*; Buckton, *Annalen*, 1859, 109, 225; Hinsberg, *Annalen*, 1887, 239, 254; Paternò and Peratoner, *Ber.*, 1889, 22, 467.
Methylmercuric iodide.	Mercury diethyl, zinc dimethyl.	Frankland, *Annalen*, 1859, 111, 57; *Jahresber.*, 1859, p. 413.
Ethylmercuric iodide.	Mercury diethyl.	Buckton, *Annalen*, 1859, 109, 222; *Jahresber.*, 1858, p. 390.
Tin diethyl di-iodide.	Tin tetraethyl.	Buckton, *ibid.*; Frankland, *Annalen*, 1859, 111, 46.
Carbon bisulphide.	Compound $ZnEt_2.CS_2$.	Grabowski, *Annalen*, 1866, 138, 165.
Chloroform.	Probably $Et.CH=CH.CH_3$ and some propylene.	Rieth and Beilstein, *Annalen*, 1862, 124, 245.
Carbon tetrachloride.	Ethylene, propylene.	do.
Bromoform.	Ethyl bromide, propylene.	Alexeyeff and Beilstein, *Bull. Soc. chim.*, 1864, [2], 2, 52; *Jahresber.*, 1864, p. 470.
Vinyl bromide.	α-Butylene.	Wurtz, *Annalen*, 1869, 152, 22; see also Chapman, *Trans. Chem. Soc.*, 1867, 20, 28; *Annalen*, 1867, 144, 255.
tert. Butyl iodide.	Trimethylethylmethane.	Goriainow, *Annalen*, 1873, 165, 107.
Allyl iodide.	Ethylene, propylene, pentane, diallyl and a hydrocarbon, C_5H_{10}.	Wurtz, *Annalen*, 1862, 123, 203; 1863, 127, 55; 1868, 148, 36; see also Wagner and Saizew, *Annalen*, 1875, 179, 304.
Methylene iodide.	Ethylene, butane.	Lwow, *J. Russ. Phys. Chem. Soc.*, 1870, 3, 170; *Jahresber.*, 1871, p. 419.

DropBooks

Reactions of Zinc Diethyl—*continued.*

Reacting Substance.	Resulting Products.	References.
Nitroethane, then water.	2-Nitrobutane, $CH_3.CH(NO_2).C_2H_5$ and N-ethyl-N-sec.-butylhydroxylamine, $CH_3.CH(C_2H_5).N(OH).C_2H_5$.	Bewad, *J. prakt. Chem.*, 1901, [2], 63, 96, 193; see also Lachman, *J. Amer. Chem. Soc.*, 1901, 23, 897; Manlock and Wolffenstein, *Ber.*, 1901, 34, 2499.
2-Nitropropane, then water.	2-Nitro-2-methyl-butane and N-ethyl-N-tert.-amylhydroxylamine.	do.
1-Bromo-1-nitroethane.	2-Nitrobutane.	Bewad, *J. Russ. Phys. Chem. Soc.*, 1888, 20, 133; *J. prakt. Chem.*, 1893, [2], 48, 336.
Alkyl nitrites, R.O.NO.	Diethylhydroxylamine, $(C_2H_5)_2N.OH$, and alcohols of type R.OH.	Bewad. *J. prakt. Chem.*, 1901, [2], 63, 95.
Nitrosobenzene.	Phenyl hydroxylamine, azoxybenzene.	Lachman, *Amer. Chem. J.*, 1899, 21, 437, 442; *J. Amer. Chem. Soc.*, 1901, 23, 901.
Paraldehyde or alkylene oxides.	No action.	Granichstädten and Werner, *Monatsh.*, 1901, 22, 323, 325.
Acetaldehyde.	Methylethylcarbinol.	Wagner, *J. Russ. Phys. Chem. Soc.*, 1876, 8, 39; *Annalen*, 1876, 181, 261.
Acrolein.	Ethylvinylcarbinol.	Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, 16, 315.
Chloral or butyrochloral.	Ethylene and corresponding primary alcohols.	Gazarolli-Thurnlakh, *Annalen*, 1881, 210, 63; 1882, 213, 369; see also Delacre, *Compt. rend.*, 1887, 104, 1184; *Bull. Soc. chim.*, 1887, [2], 48, 784.
Dichloroacetal.	Ethyl chloride, propylene, diethyl ether.	Paternò, *Annalen*, 1869, 150, 134.
Acetone.	Mesityl oxide and other condensation products.	Pawlow, *Annalen*, 1877, 188, 130.
Chlorodimethyl ether. Similar reaction with chloromethylethyl ether.	Methylpropyl ether.	Henry, *Compt. rend.*, 1891, 113, 369; *Bull. Soc. chim.*, 1892, [3], 7, 150.
Diethyl oxalate or ethyl oxalyl chloride.	α-Oxydiethyl-acetic ethyl ester.	Frankland, *Annalen*, 1863, 126, 109; Frankland and Duppa, *Annalen*, 1865, 135, 29; Henry, *Ber.*, 1872, 5, 950.
Malonic ester.	Phloroglucin dicarboxylic acid diethyl ester.	Lang, *Ber.*, 1886, 19, 2938; see also Moore, *Trans. Chem. Soc.*, 1904, 85, 165.

Reactions of Zinc Diethyl—*continued.*

Reacting Substance.	Resulting Products.	References.
Acetyl chloride.	Methyldiethylcarbinol or methylethyl ketone.	Freund, *Annalen*, 1861, 118, 3; Butlerow, *Zeitsch. Chem.*, 1865, p. 614.
Isobutyryl chloride, then water.	Ethylene, ethylisopropyl ketone, ethylisopropyl carbinol, diethylisopropyl carbinol.	Grigorowitsch and Pawlow, *J. Russ. Phys. Chem. Soc.*, 1891, 23, 162.
Benzoyl chloride.	Ethylphenyl ketone.	Freund, *Annalen*, 1861, 118, 20; Kalle, *Annalen*, 1861, 119, 165.
Acetic anhydride.	Methylethyl ketone.	Granichstädten and Werner, *Monatsh.*, 1901, 22, 315.
Acetamide.	Zinc acetamide. $Zn(NH.CO.CH_3)_2$, ethane.	Frankland, *Jahresber.*, 1857, p. 419; Gal, *Bull. Soc. chim.*, 1883, [2], 39, 647.
Oxamide.	Zinc oxamide, ethane.	do.
Ethylamine.	Ethane, compound $Zn(NH.C_2H_5)_2$.	Gal, *Bull. Soc. chim.*, 1883, [2], 39, 583.
Diethylamine.	Compound $Zn[N(C_2H_5)_2]_2$.	Frankland, *Jahresber.*, 1857, p. 419.
Triethylamine or triethylphosphine.	No action.	Gal, *loc. cit.*
Diphenylnitrosamine.	Diethylhydroxylamine.	Lachman, *Amer. Chem. J.*, 1899, 21, 436; *Ber.*, 1900, 33, 1022; see also Japp and Wilcox, *Trans. Chem. Soc.*, 1880, 37, 665; Japp and Miller, *Trans. Chem. Soc.*, 1881, 39, 224.
Tetraethyl ester of orthosilicic acid and sodium.	Triethylsilicane, tetraethylsilicane, triethylsilicyl ethyl ether, diethyl diethoxysilicane, ethyl triethoxysilicane.	Ladenburg, *Annalen*, 1872, 164, 301.

DropBooks

Zinc dipropyl, $Zn(C_3H_7)_2$, is obtained as follows :—

1. By heating mercury dipropyl and zinc in a sealed tube at 120° to 130° C.[1]

2. By heating propyl iodide and zinc turnings under a reflux condenser at 130° C.[2] Yield 30 per cent.

3. By heating together propyl iodide and zinc copper couple, then distilling the reaction mixture in a stream of carbon dioxide. Yield 75 per cent.[3]

[1] Cahours, *Compt. rend.*, 1873, 76, 135, 751; *Jahresber.*, 1873, p. 518.
[2] Pape, *Ber.*, 1881, 14, 1873.
[3] Gladstone and Tribe, *Ber.*, 1873, 6, 1136; see also Henry, *Compt. rend.*, 1891, 113, 370.

4. Propyl iodide, 140 grams, and 5 grams of sodium zinc alloy are heated with 280 to 350 grams of zinc turnings for four to five days on the water-bath. Distillation of the product gives a 43 to 50 per cent. yield of zinc dipropyl.[1]

Zinc dipropyl is a colourless, heavy liquid of very unpleasant smell, and its boiling-point differs according to the various investigators as follows: 146° C. (Gladstone and Tribe); 148° C. (Schtscherbakoff); 150° C. (Pape); 158° to 160° C. (Cahours). It undergoes the following reactions:—

1. Decomposed by water, with evolution of propane.

2. With *phosphorus and arsenic trichlorides* it yields tripropylphosphine and tripropylarsine respectively.

3. With trichlorosilicane it gives tripropyl and tetrapropylsilicanes.[2]

4. With tin tripropyl iodide, tin tetrapropyl is formed.

5. With acetaldehyde, ethyl alcohol and methylpropylcarbinol are formed.[3]

6. Chlorodimethyl ether with zinc dipropyl yields methyl-n-butyl ether.[4]

7. With acetyl chloride, methylpropylcarbinol is formed and propylene evolved.[5] In a similar way butyryl chloride gives dipropyl carbinol.[6]

Zinc di-isopropyl, $Zn(C_3H_7)_2$, results as follows:—

1. Isopropyl iodide and zinc copper couple are heated at 50° C. and finally at 100° C.[7]

2. Isopropyl iodide (170 grams) in 100 grams of ether are heated for nine hours with 100 grams of zinc and 2 to 3 grams of sodium zinc alloy on a boiling water-bath, and the product distilled from an oil bath in a stream of carbon dioxide.[8]

3. Isopropyl iodide (125 grams) and 140 grams of zinc dust are added to a large quantity of zinc turnings and the whole heated at 40° C. on the water-bath. Yield 25 per cent.[9]

Zinc di-isopropyl is a mobile liquid, fuming strongly in air and readily oxidised to zinc di-isopropylate, $Zn(OC_3H_7)_2$. It boils with some decomposition at 135° to 137° C., but without decomposition at 94° to 98° C. at 40 mm. It inflames when a large surface is exposed to the atmosphere.

Zinc di-isobutyl, $Zn(C_4H_9)_2$, may be prepared by the following methods:—

1. By heating mercury di-isobutyl and zinc in a sealed tube at 130° to 150° C.[10]

[1] Schtscherbakoff, *J. Russ. Phys. Chem. Soc.*, 1881, 13, 350; *Jahresber.*, 1881, p. 890; *Ber.*, 1881, 14. 1710.

[2] Pape, *Annalen*, 1884, **222**. 359; *Ber.*, 1881, 14. 1873.

[3] Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, 16, 283.

[4] Henry, *Bull. Soc. chim.*, 1892, [3], 7, 150.

[5] Markownikoff, *J. Russ. Phys. Chem. Soc.*, 1883, 15, 406; *Ber.*, 1883, 16, 2284; see also Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, 16, 336; Garzarolli-Thurnlackh, *Annalen*, 1884, 223, 164.

[6] Schtscherbakoff, *J. Russ. Phys. Chem. Soc.*, 1881, 13, 343; *Jahresber.*, 1881, p. 890; see also Bogomolez, *Annalen*, 1881, 209, 92.

[7] Gladstone and Tribe, *Ber.*, 1873, 6, 1136.

[8] Ragosin, *J. Russ. Phys. Chem. Soc.*, 1892, 24, 550.

[9] Bohm, *J. Russ. Phys. Chem. Soc.*, 1899, 31. 46.

[10] Cahours, *Compt. rend.*, 1873, 77, 1406; *Bull. Soc. chim.*, 1874, [2], 21, 357; *J. prakt. Chem.*, 1836, [2], 8, 398; Marquardt, *Ber.*, 1888, 21, 2038.

2. By heating zinc with isobutyl iodide for eight to ten hours on a water-bath, until gas evolution ceases, then rapidly distilling the product.[1] Yield 35 to 41 per cent.

3. By heating zinc and isopropyl iodide for sixty hours under a pressure of 30 mm. on a water-bath, then distilling off the product in an atmosphere of hydrogen.[2]

Zinc di-isobutyl is a liquid, B.pt. 165° to 167° C., less readily oxidised than zinc dipropyl. It reacts vigorously with trihalides of phosphorus and arsenic, yielding corresponding phosphines and arsines. With acetaldehyde it forms principally ethyl alcohol, but also a little isobutyl alcohol,[3] and with isovaleryl chloride it gives di-isobutyl ketone.[4]

Zinc di-isoamyl, $Zn(C_5H_{11})_2$, is prepared either by heating isoamyl iodide and zinc at 180° C.[5] or by heating mercury di-isoamyl and zinc in a sealed tube at 130° C.[6] It is a liquid, fuming in air and boiling at 220° C. and has a density of 1·022 at 0° C. With acetaldehyde it forms methylisoamyl carbinol, isoamyl alcohol, and ethyl alcohol.[7]

Zinc methyl methylate, $CH_3.Zn.OCH_3$, is obtained by dissolving zinc dimethyl in methyl iodide and passing air through the mixture or by treating zinc dimethyl with a little methyl alcohol.[8] It forms a camphor-like, crystalline mass, usually containing some zinc dimethylate, $Zn(OCH_3)_2$, and is decomposed by water into methane, methyl alcohol, and zinc hydroxide.

Zinc methyl ethylate, $CH_3.Zn.OC_2H_5$, is formed from zinc dimethyl and the tetraethyl ester of orthosilicic acid.[9] It is a crystalline compound, decomposed by water, with separation of zinc hydroxide.

Zinc ethyl iodide, $C_2H_5.ZnI$, may be isolated by the following methods :—

DropBooks

1. Ethyl iodide, zinc turnings, and a little zinc diethyl are allowed to stand in a sealed tube for about a week at room temperature.[10]

2. Ethyl iodide and zinc-copper couple are heated under reflux on a water-bath for thirty to sixty minutes.[11]

3. Equivalent quantities of zinc and ethyl iodide are mixed with an equal volume of ether in a reflux apparatus, the air replaced by carbon dioxide, and the mixture heated until all the zinc dissolves. The ether is then evaporated off, leaving the zinc ethyl iodide as a crystalline mass.[12]

Zinc ethyl iodide is a white crystalline product which decomposes into zinc diethyl and zinc iodide when distilled in a stream of carbon dioxide. The following are some of the reactions carried out with zinc ethyl iodide :—

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[1] Garzarolli-Thurnlackh and Popper, *Annalen*, 1884, 223, 168.
[2] Ponzio, *Gazzetta*, 1900, 30, ii. 23 ; *Chem. Zentr.*, 1900, ii. 624.
[3] Ssokoloff, *J. Russ. Phys. Chem. Soc.*, 1887, 19, 203 ; *Jahresber.*, 1887, p. 1351.
[4] Ponzio, *Gazzetta*, 1905, 35, ii. 394.
[5] Frankland, *Annalen*, 1853, 85, 360.
[6] Frankland and Duppa, *Annalen*, 1864, 130, 122 ; Marquardt, *Ber.*, 1888, 21, 2038.
[7] Ssokoloff, *J. Russ. Phys. Chem. Soc.*, 1887, 19, 203 ; *Jahresber.*, 1887, p. 1351.
[8] Butlerow, *Jahresber.*, 1864, p. 467.
[9] Ladenburg, *Annalen*, 1874, 173, 148.
[10] Filetl and Cantapulo, *Gazzetta*, 1892, 22, ii. 388 ; Lachman, *Amer. Chem. J.*, 1900, 24, 33.
[11] Lachman, *ibid.*
[12] Michael, *Amer. Chem. J.*, 1901, 25 423 ; see Job and Reich, *Bull. Soc. chim.*, 1923 33, [iv.], 1414.

1. When heated with powdered tin it forms tin tetraethyl.[1]

2. With isobutyl iodide it gives trimethylethylmethane, ethylene, and isobutylene.[2]

3. With allyl iodide it yields ethyl iodide, diallyl, methylethylethylene, ethylene, propylene.[3]

4. Zinc ethyl iodide with nitro-ethane gives β-ethyl-β-sec-butylhydroxylamine,[4] and with isoamyl nitrite, $\beta.\beta$-diethylhydroxylamine.

5. With chloroacetyl chloride it gives the chloroacetic ester of chloromethyldiethylcarbinol, $CH_2Cl.C(C_2H_5)_2.O.CO.CH_2Cl$;[5] with butyryl chloride it forms hexanon-(3);[6] with benzoyl chloride, ethyl phenyl ketone is obtained.[7] and with benzene sulphonic chloride, the main product is zinc benzene sulphinate and a little sulphone.

6. Zinc ethyl iodide and diethyl malonate yield ethyl-diethyl malonate and some diethyl ester of diethyl malonic acid.[8]

7. Zinc ethyl iodide does not react with carbon dioxide.[9]

Zinc ethyl trichloroethylate, $C_2H_5.Zn.O.CH_2.CCl_3$, is obtained by the action of zinc diethyl on chloral in ethereal solution.[10] The compound is crystalline. and with water yields trichloro-ethyl alcohol.

Zinc isopropyl iodide, $(CH_3)_2CH.ZnI$.—Zinc and isopropyl iodide are heated together and the product extracted with ether.[11] With isoamyl nitrite it yields N.N-di-isopropyl hydroxylamine, and with nitroethane, N-isopropyl-N-($\alpha.\beta$-dimethylpropyl)-hydroxylamine is obtained.

Zinc diphenyl, $ZnPh_2$.[12] is obtained by boiling mercury diphenyl and zinc for two minutes in an atmosphere of hydrogen. On cooling, rosettes of crystals of zinc diphenyl separated, M.pt. 105° C. The compound is dried in a vacuum apparatus at 80° C. in hydrogen atmosphere; it then melts (in hydrogen) sharply at 105° to 106° C. Zinc diphenyl is susceptible to air and light, and in presence of water yields zinc hydroxide and benzene. In dry air it decomposes into zinc oxide and diphenyl. It inflames with fuming nitric acid. In hydrogen, zinc diphenyl boils under ordinary pressure at 280° to 285° C. with slight decomposition. It is easily soluble in benzene, ether, and light petroleum, also in chloroform with evolution of heat. When the reaction product from the chloroform solution is decomposed with dilute nitric acid there is much chlor-ion in solution, and triphenylmethane may be isolated from the chloroform solution. From an iodine solution of zinc diphenyl, phenyl zinc iodide is obtained. Zinc diphenyl heated with fifteen atomic proportions of mercury for ten minutes gives only traces of mercury diphenyl.

[1] Letts and Collie, *Jahresber.*, 1886, p. 1601.
[2] Ssimonowitsch, *J. Russ. Phys. Chem. Soc.*, 1899. 31, 41; *Chem. Zentr.*, 1899, i. 1066.
[3] Gwosdow, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 340; *Chem. Zentr.*, 1903, ii. 339.
[4] Bewad, *Ber.*, 1907, 40, 3072; *J. Russ. Phys. Chem. Soc.*, 1907, 39, 958; *Chem. Zentr.*, 1908, i. 115.
[5] Blaise and Herman, *Ann. Chim. Phys.*, 1911, [8], 23, 522.
[6] Michael, *Ber.*, 1906, 39, 2144.
[7] Michael, *Amer. Chem. J.*, 1901, 25, 423.
[8] Michael, *ibid.*, 424.
[9] Zelinsky, *Ber.*, 1902, 35, 2694.
[10] Garzarolli-Thurnlackh, *Annalen*, 1881. 210, 64; Delacre, *Bull. Soc. chim.*, 1887, [2], 48. 785.
[11] Bewad, *Ber.*, 1907, 40, 3066; *J. Russ. Phys. Chem. Soc.*, 1907, 39, 950; *Chem. Zentr.*, 1908, i. 115.
[12] Hilpert and Grüttner, *Ber.*, 1913, 46, 1675.

The physical constants for some mixed zinc alkyls [1] are given in the Appendix, Table I.

Cadmium.[2]

Löhr [3] from metallic cadmium and methyl iodide obtained a small quantity of cadmium methyl, but he was unable to purify it. Wanklyn [4] also obtained a small amount of liquid, undoubtedly cadmium diethyl, by the interaction of ethereal ethyl iodide and metallic cadmium. These compounds have since been obtained in good yields from cadmium halides and alkyl magnesium halides. Since the compounds are oxidised in air and affected by moisture, the Grignard solutions cannot be decomposed by water, but are distilled directly, and the product purified by fractionation under reduced pressure. The boiling-points are high compared with those of the mercury dialkyls. This is not due to association, since the molecular weights determined by the freezing-point method indicate single molecules, and the vapour density of the methyl compound is normal. The pure cadmium dialkyls are colourless, strongly refracting liquids, for the most part crystalline on strong cooling. They possess an unpleasant musty odour, and have a metallic taste. The low molecular compounds, especially the methyl derivative, are extremely volatile at ordinary temperatures, their vapours irritating the mucous membrane of the nose. They volatilise along with ether vapour, especially cadmium dimethyl, so that the complete separation, in spite of the wide difference of boiling-point, only succeeds with appreciable loss, even when a fractionating column is used. This bears a resemblance to zinc dimethyl which gradually decomposes on distillation.[5] In a nitrogen atmosphere in the dark, cadmium dialkyls may be kept for a month without decomposition. In the presence of traces of air or moisture they become coloured, particularly rapidly in the light, when they change to steely-blue, and a black deposition of metal occurs. The methyl compound gives a white precipitate. When poured upon a watch-glass they oxidise rapidly without inflaming, giving off brown fumes. They carbonise filter paper, which ultimately glows. They inflame under suitable conditions, and do so with hissing when drained from a pipette. Cadmium dimethyl differs from all other cadmium dialkyls in its oxidisability. It fumes less in air and becomes coated only with a white crust of methylate. In water the compounds sink, and when shaken slowly decompose with a crackling noise, continuing thus for hours. With most organic solvents they are miscible, the solutions in air becoming covered with a white film. Pure cadmium dialkyls can be heated in an indifferent gas-stream to 150° C. without decomposition. At slightly higher temperatures they begin to decompose with evolution of gas and deposition of black metallic cadmium, and at 180° C. they explode.

Cadmium dimethyl, $CdMe_2$.—Twenty-nine grams (1·2 mols.) of magnesium and the requisite amount of methyl bromide are dissolved in 350 c.c. of ether, and 136 grams (0·5 mol.) of finely powdered, anhydrous cadmium bromide introduced in small quantities, with good shaking and

[1] Krause and Fromm, *Ber.*, 1926, 59, [B], 931.
[2] Krause, *Ber.*, 1917, 50, 1813.
[3] Löhr, *Annalen*, 1853, 87, 55.
[4] Wanklyn, *Quart. J. Chem. Soc.*, 1856, 9, 193; *Jahresber.*, 1856, p. 554
[5] Frankland, *Annalen*, 1859, 111, 62.

without cooling. When the reaction is complete, the majority of the ether is distilled off in a stream of nitrogen, using a fractionating column, and a temperature not above 80° C. The residue is distilled from an oil bath, in nitrogen, at a pressure of 13 mm., the ether and cadmium methyl being collected in a receiver cooled in liquid air or carbon dioxide-ether mixture. After one hour the temperature is raised to 120° C. The product is fractionated to remove the ether, then distilled in nitrogen at ordinary pressure. At 105·6° C. 60 grams of pure cadmium methyl are obtained. Yield 85 per cent. When poured into water it sinks, evolving methane and giving a precipitate of cadmium hydroxide. When cooled it solidifies, melting at −4·5° C., the crystals taking the form of star-shaped rods when the product is distilled under reduced pressure into a receiver cooled in liquid air.

The following cadmium alkyls may be prepared in a similar manner, the yields being shown in each case :—

Cadmium diethyl, 90 per cent. ; **cadmium di-n-propyl**, 85 per cent. ; **cadmium di-n-butyl**, 70 per cent. ; **cadmium di-isobutyl**, 75 per cent. ; **cadmium di-isoamyl**, 55 per cent.

The physical constants of these compounds are shown in the Appendix, Tables II. and III.

Cadmium diphenyl, $CdPh_2$,[1] may be obtained by heating metallic cadmium and mercury diphenyl in an atmosphere of hydrogen. It is stable in the dry state, but becomes discoloured when kept in a vacuum desiccator for an hour. When air is passed through its benzene solution several colour changes take place, and a reddish-brown body is finally precipitated. With water the brown solution is decolorised and cadmium hydroxide precipitated. Cadmium diphenyl quickly decolorises iodine solution, and the cadmium may be replaced by mercury or zinc with formation of mercury and zinc diphenyl.

[1] Hilpert and Grüttner, *Ber.*, 1913, 46, 1675.

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CHAPTER III.

MERCURY.

Alkyl Compounds of the Types R_2Hg and RHgX.

The early workers on the type R_2Hg prepared their compounds by making use of dilute sodium amalgams. The alkyl iodides were shaken with an excess of sodium amalgam, containing 0·2 to 0·25 per cent. of sodium, in the presence of methyl or ethyl acetate, the latter acting as a catalyst. In this way the following derivatives were produced, methyl, ethyl, n-propyl, isobutyl, isoamyl, and n-octyl. The reaction takes place readily at ordinary temperatures and is very vigorous in the case of the lower members of the series. Since the discovery of the Grignard reagent, the above method of preparation has been abandoned, and practically all the compounds have since been isolated by the interaction of magnesium alkyl halides and mercury halides. Amongst other methods of preparation devised for the production of these compounds the following are of interest. Mercury dimethyl has been formed from methyl mercuric iodide (type RHgX) by distillation with potassium hydroxide or cyanide, calcium hydroxide, zinc methyl or granulated zinc, or by boiling its pyridine solution with metallic copper. Methyl mercuric acetate in the presence of pyridine when subjected to electrolysis yields mercury dimethyl, also the action of aluminium carbide on a dilute hydrochloric acid solution of mercuric chloride. Mercury diethyl has been obtained from methyl or allyl mercuric iodides by treating them with zinc ethyl and also from α-naphthyl mercuric bromide and ethyl magnesium bromide. The latter reaction was carried out in an attempt to produce mercury ethyl α-naphthyl. Triethylbismuthine is decomposed by mercuric chloride, the mercury replacing the bismuth, forming mercury diethyl. The only case when mercuric oxide is used in the formation of the type R_2Hg is its interaction with ethyl hydrazine to produce mercury diethyl. Mercury di-sec-butyl has been formed by the electrolysis of methyl ethyl ketone using a mercury cathode.

All the compounds of the type R_2Hg are liquids; the methyl and ethyl derivatives are volatile at ordinary temperatures, and are said to be very poisonous. Mercury dimethyl, diethyl, and di-n-propyl may be distilled under ordinary pressure without decomposition; mercury di-isopropyl, di-n-butyl, di-isobutyl and di-sec-butyl, have only been distilled under reduced pressure; mercury di-tert-butyl and di-tert-amyl show considerable decomposition even when distilled at 5 mm.; mercury di-isoamyl also undergoes decomposition when distilled *in vacuo*, but is volatile in steam, whilst mercury di-sec-octyl cannot be distilled at all, since it decomposes even at 3 mm.

Mercury di-isobutyl and di-isoamyl react with halogens to form halides of the type RHgX, and mercury diethyl gives similar results

except that it inflames with chlorine. Iodine reacts with mercury dimethyl, di-n-propyl, di-sec-butyl, and di-n-octyl to yield the corresponding iodides, RHgI.

With acids, mercury dimethyl, diethyl, and di-n-propyl form salts of the type RHgX, but mercury di-isoamyl is decomposed by glacial acetic acid.

By electrolysing methyl or ethyl mercuric halides in liquid ammonia solution the complexes, MeHg- and EtHg- are obtained as black deposits on the cathode, which show metallic reflexion and have a high electrical conductivity.

The mercury may be replaced from mercury dimethyl by sodium, magnesium, zinc, or aluminium under suitable condition with formation of organometallic compounds of these metals; with mercury diethyl, the reaction takes place with sodium, magnesium, cadmium, beryllium, zinc, aluminium, bismuth, and tellurium; with mercury di-n-propyl, the metals sodium, beryllium, zinc and aluminium react, and sodium also reacts with mercury di-n-octyl.

Phosphorus trichloride, stannous chloride, and mercuric iodide give products of the type RHgX with mercury dimethyl, but cadmium iodide does not yield the above type, and antimony trichloride yields an organometallic compound. Mercury diethyl reacts with the trichlorides of phosphorus, arsenic, and antimony to yield organo derivatives of these elements, and with mercuric chloride it gives ethyl mercuric chloride.

Some of the methods by which the type RHgX may be prepared are outlined in the above discussion of the type R_2Hg. In contrast to the compounds just discussed, all derivatives of the type RHgX are solids. It has been pointed out that a number of the halides may be obtained by the direct action of halogens. Others may be formed from the corresponding hydroxides by the action of acids, whilst tert-butyl, tert-amyl, and sec-octyl mercuric bromides are prepared by treating the magnesium alkyl halides with an excess of mercuric bromide. Magnesium n-butyl bromide with an excess of mercuric chloride gives equal parts of the chloride and bromide. The halides, especially the iodides, may be converted to the hydroxides by moist silver oxide, and in the case of the methyl and ethyl compounds they may be obtained direct from the R_2Hg type by the action of potassium permanganate.

It was discovered as early as 1852 that mercury combines with methyl iodide in sunlight to form methyl mercuric iodide, and a similar reaction takes place with ethyl iodide, but owing to the tendency of ethyl mercuric iodide to decompose in direct sunlight, the operation must be conducted in diffused light. The n-propyl and isobutyl iodides also react with mercury to give the corresponding iodides. The reaction, however, is much more rapid with the unsaturated alkyl and propargyl iodides, whilst with methylene iodide it only goes to completion after several days. Methyl mercuric iodide has also been formed by treating magnesium methyl iodide with an excess of mercuric chloride.

Alkyl Compounds of the Type R_2Hg.

Mercury dimethyl, $HgMe_2$, may be prepared:

1. By the distillation of a mixture of methyl mercuric iodide and solid potassium cyanide.[1]

[1] Buckton, *Annalen*, 1858, 108, 103: *Jahresber.*, 1858, p. 388.

2. The same compound is isolated when the potassium cyanide is replaced by potassium or calcium hydroxide.

3. By the distillation of methyl mercuric iodide and zinc dimethyl.[1]

4. By the distillation of methyl mercuric iodide and granulated zinc.[2]

5. A mixture of 10 parts of methyl iodide and 1 part of methyl acetate is shaken with an excess of 0·2 per cent. sodium amalgam, the whole being kept cool as the reaction is very violent during its initial stages.[3]

6. Mercuric chloride is dissolved in a very dilute aqueous solution of hydrochloric acid and an equal weight of aluminium carbide added, mercury dimethyl soon separates.[4]

7. By action of the Grignard reagent on mercuric chloride.[5] In this reaction it is necessary to remove any unchanged magnesium from the Grignard solution before the addition of the mercuric chloride, otherwise some reduction to mercurous salt occurs, the yield being consequently lowered. Yield 61 per cent.

8. The most satisfactory method so far described for the preparation of mercury dimethyl consists in subjecting an aqueous solution of methyl mercuric acetate containing pyridine to electrolysis.[6] This process gave a yield of 92 per cent.

9. By treating methylmercuric iodide in pyridine solution with metallic copper.[7]

The compound is a colourless liquid having a faint sweetish odour, is easily inflammable and a very deadly poison; B.pt. 93° to 96° C., density 3·069; 2·95412 at 22·2° C. It is readily soluble in alcohol or ether, insoluble in water. The following values were found for the refractive index by Ghira:[8] n_α 1·52780; n_γ 1·55588; n_D 1·53266 at 22·2° C. The following physical constants are due to Krause:[9] B.pt. 92° at 761 mm., density 3·0836 at 19·2° C., $n_{H\alpha}$ 1·54212, n_D 1·54735, $n_{H\beta}$ 1·56052, n_{H_γ} 1·57177 at 16·8° C. From these the following were calculated: $MR_{H\alpha}$ 23·528; MR_D 23·717; $M\Delta_{\gamma-\alpha}$ 1·058; $M\Delta_{\beta-\alpha}$ 0·659; $AR_{H\alpha}$ 12·148; AR_D 12·282; $A\Delta_{\gamma-\alpha}$ 0·773; $A\Delta_{\beta-\alpha}$ 0·472. The molecular heat of combustion at constant volume is 430,800 calories,[10] and work on the dielectric constant has been carried out by Matthews,[11] and studies of the absorption spectra by Crymble.[12] The complex MeHg- has been isolated [13] by electrolysing methyl mercuric halides in liquid ammonia solution. It forms a fine black deposit on the cathode, and may be obtained in the form of flakes if the process be carried out in water or alcohol solution. The latter form appears to be more stable than the former, which decomposes into mercury and

[1] Buckton, *Annalen*, 1859, 109, 222; *Jahresber.*, 1858, p. 390; *J. prakt. Chem.*, 1859, [1], 76, 362.
[2] Buckton, *Trans. Chem. Soc.*, 1863, 16, 21; *Jahresber.*, 1863, p. 469.
[3] Frankland and Duppa, *Trans. Chem. Soc.*, 1863, 16, 415; *Annalen*, 1864, 130, 104.
[4] Hilpert and Ditmar, *Ber.*, 1913, 46, 3738.
[5] Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153.
[6] Maynard and Howard, *Trans. Chem. Soc.*, 1923, 123, 960.
[7] Hein, Wayler, and Retter, *Ber.*, 1925, 58, [B], 1506.
[8] Ghira, *Atti. R. Accad. Lincei*, 1894, [5], 3, i. 298; *Gazzetta*, 1894, 24, i. 311.
[9] Krause, *Ber.*, 1926, 59, [B], 935.
[10] Berthelot, *Compt. rend.*, 1899, 129, 918.
[11] Matthews, *Chem. Zentr.*, 1906, i. 224.
[12] Crymble, *Trans. Chem. Soc.*, 1914, 105, 658.
[13] Kraus, *J. Amer. Chem. Soc.*, 1913, 35, 1732.

mercury dimethyl at room temperature. The deposits have a high conductivity and exhibit metallic reflexion.

Mercury dimethyl undergoes reactions with various substances as indicated in the following table :—

REACTIONS OF MERCURY DIMETHYL.

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Halogens, *e.g.* iodine.	Alcoholic solution.	Methyl mercury iodide; methyl iodide.	Buckton, *Annalen*, 1858. 108, 103; Frankland and Duppa, *Trans. Chem. Soc.*, 1863, 16, 415; *Annalen*, 1864, 130, 104; Hilpert and Ditmar, *Ber.*, 1913. 46, 3738.
Cyanogen iodide.	Ether solution at 50° C.	Mercuric cyanide.	Calmels, *Compt. rend.*, 1884, 99, 240.
	Ether solution at 110° C.	Mercuric iodide, methyl isocyanide.	
Concentrated sulphuric or hydrochloric acids.	..	Methane, methyl mercuric salts.	Buckton, *ibid.*
Glacial acetic acid.	120–130° C. for 1 hour.	Methane, methyl mercuric acetate.	Otto, *Annalen*, 1870, 154, 198.
	250° C. for 16 hours.	Metallic mercury, brown amorphous product.	Jones and Werner, *J. Amer. Chem. Soc.*, 1918, 40, 1257.
Nitrogen peroxide.	..	Imido dihydroximic acid.	Bamberger, *Ber.*, 1899, 32, 3546; Bamberger and Müller, *Ber.*, 1899, 32, 3549.
	Ether solution at −20° C.	Dioxybiuret, methyl mercuric nitrate.	
Phosphorus trichloride.	..	Methyl mercuric chloride.	Buckton, *loc. cit.*
Antimony trichloride.	..	Methyl mercuric chloride, mercury, trimethylstibine dichloride.	Buckton, *Trans. Chem. Soc.*, 1863, 16, 22; *Jahresber.*, 1863, p. 470; Landolt, *Annalen*, 1851, 78, 91.
Mercuric iodide.	..	Methyl mercuric iodide.	Buckton, *Annalen*, 1858, 108, 105.
Cadmium iodide.	..	Methane, mercury, mercuric iodide.	Löhr, *Annalen*, 1891, 261, 48.
Stannous chloride.	..	Crystalline product yielding methyl mercuric chloride and a tin compound with water.	Buckton, *loc. cit.*
Potassium permanganate.	..	Methyl mercuric hydroxide (?) (not isolated).	Seidel, *J. prakt. Chem.*, 1884, [2]. 29, 135.
Thiodimethylanilline.	Sealed tube at 150–210° C.	Metallic mercury, grey product not analysed.	Holzmann, *Ber.*, 1888, 21, 2071.

Reactions of Mercury Dimethyl—*continued.*

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Sodium.	Alcoholic solution.	Mercury, gas evolved.	Chapman, *Trans. Chem. Soc.*, 1866, 19, 150; *Annalen*, 1866, 139, 128.
	Inert solvents.	Sodium methyl.	Schlenk, *Ber.*, 1917, 50, 262.
Sodium and carbon dioxide.	Ether solution.	Traces of sodium acetate.	Schorigin, *Ber.*, 1908, 41, 2722.
Cadmium.	..	Methane, cadmium amalgam.	Löhr, *loc. cit.*
Magnesium.	Sealed tube at 130° C. for 36 hours.	Metallic mercury, magnesium dimethyl.	Löhr, *loc. cit.*; Fleck, *Annalen*, 1893, 276, 130.
Zinc.	Sealed tube at 120° C.	Metallic mercury, zinc dimethyl.	Frankland and Duppa, *Trans. Chem. Soc.*, 1864, 17, 28; *Annalen*, 1864, 130, 117.
Aluminium.	Sealed tube at 100° for several hours.	Aluminium trimethyl.	Buckton and Odling, *Annalen Suppl.*, 1865-1866, 109; *Proc. Roy. Soc.*, 1865, 14, 19. Cahours, *Annalen*, 1860, 114, 243.

Mercury diethyl, $HgEt_2$, is obtained as follows :—

1. By the distillation of ethyl mercuric chloride with potassium cyanide. The yield is very small.[1]

2. By the addition of mercuric or mercurous chloride to cooled zinc diethyl.[1]

3. By the distillation of ethyl mercuric iodide with zinc diethyl.[1]

4. From methyl mercuric iodide and zinc diethyl, the other products of reaction being zinc dimethyl and zinc iodide.[2]

5. From allyl mercuric iodide and zinc diethyl in cold ether, the reaction yielding, in addition, diallyl and mercury.[3]

6. By the interaction of 2 per cent. sodium amalgam and ethyl iodide, using ethyl acetate as a catalyst.[4] The ethyl iodide may be replaced by ethyl bromide.[5]

7. From ethyl mercuric chloride and alkaline stannous chloride solution.[6]

8. From α-naphthyl mercuric bromide and ethyl magnesium bromide.[7]

9. Formed in small quantity when ethyl hydrazine is acted upon by mercuric oxide.[8]

[1] Buckton, *Annalen*, 1858, 108, 103; 1859, 109, 218; *Jahresber.*, 1858, p. 389.
[2] Frankland, *Annalen*, 1859, 111, 57; *Jahresber.*, 1859, p. 413.
[3] Linnemann, *Annalen*, 1866, 140, 180; Krassowski, *Ber.*, 1870, 3, 625; Oppenheim, *Ber.*, 1871, 4, 671.
[4] Frankland and Duppa, *Trans. Chem. Soc.*, 1863, 16, 418, 424; *Annalen*, 1864, 130, 109, 117.
[5] Chapman, *Trans. Chem. Soc.*, 1866, 19, 150; *Annalen*, 1866, 139, 138.
[6] Dimroth, *Chem. Zentr.*, 1901, i. 451; *Ber.*, 1902, 35, 2853.
[7] Hilpert and Grüttner, *Ber.*, 1915, 48, 908.
[8] Fischer, *Annalen*, 1879, 199, 332

10. By the action of mercuric chloride on bismuth triethyl.[1]

11. From ethyl magnesium bromide and mercuric chloride. Yield 60 to 63 per cent.[2]

12. By treating ethyl mercuric chloride in pyridine solution with metallic copper.[3]

Mercury diethyl is a liquid of penetrating odour and appreciably volatile at ordinary temperature. It boils at 159° C., has a density of 2·42346 at 23·2° C. and is readily soluble in ether, less soluble in alcohol, and insoluble in water. The following physical constants have been determined: Refractive index, $n_{H\alpha}$ 1·53519; n_D 1·53990; $n_{H\gamma}$ 1·56240 at 23·2° C.[4] Physical constants by Krause:[5] B.pt. 57° C. at 16 mm., density 2·4660 at 20° C., $n_{H\alpha}$ 1·54285, n_D 1·54765, $n_{H\beta}$ 1·55990, $n_{H\gamma}$ 1·57048, $MR_{H\alpha}$ 33·018, MR_D 33·262, $M\Delta_{\gamma-\alpha}$ 1·386, $M\Delta_{\beta-\alpha}$ 0·857, $AR_{H\alpha}$ 12·442, AR_D 12·591. $A\Delta_{\gamma-\alpha}$ 0·873, $A\Delta_{\beta-\alpha}$ 0·530. Molecular heat of combustion at constant volume, 733,600 calories.[6] Investigations on the dielectric constant have been carried out by Walden,[7] and the complex C_2H_5Hg- was isolated by Krause in a similar manner to the corresponding methyl body. Whilst mercury dimethyl possesses much the same absorptive power as mercuric chloride, the diethyl compound shows much greater absorption.[8]

Reactions.—The action of various substances on mercury diethyl is shown in the following table :—

REACTIONS OF MERCURY DIETHYL.

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Chlorine.	..	Mercury diethyl inflames.	Buckton, *Annalen.* 1859, 112, 221; *Jahresber.*, 1859, p. 408.
Bromine or Iodine.	Aqueous solution.	Ethyl mercuric halides, ethyl halides.	do.
Hydrochloric or sulphuric acid.	Heat.	Ethyl mercuric salts, ethane.	Buckton, *loc. cit.*; *Annalen*, 1858, 109, 220; *Jahresber.*, 1858, p. 390; *J. prakt. Chem.*, 1860, 1, 79; Schorlemmer, *Annalen*, 1864, 132, 234.
Glacial acetic acid.	Heat at 220° C. for 16 hours. Heat at 120° C. for 1 hour.	Ethyl acetate, mercury, ethane, ethylene. Ethyl mercuric acetate.	Jones and Werner, *J. Amer. Chem. Soc.*, 1918, 40, 1257. Otto, *Annalen*, 1870, 154, 198.
Bromacetic ester.	Heat at 150° C. for 8 hours.	Ethyl mercuric bromide, traces of ethyl acetate.	Sell and Lippmann, *J. prakt. Chem.*, 1866, (1), 99, 432.

[1] Dünhaupt, *J. prakt. Chem.*, 1854, [1], 61, 423; *Annalen*, 1854, 92, 379.
[2] Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153.
[3] Hein, Wagler, and Retter, *Ber.*, 1925, 58, [B], 1506.
[4] Ghira, *Atti. R. Accad. Lincei*, 1894, [5], 3, 1. 298; *Gazzetta*, 1894, 24, 1. 311.
[5] Krause, *Ber.*, 1926, 59, [B], 935.
[6] Berthelot, *Compt. rend.*, 1899, 129, 918.
[7] Walden, *Zeitsch. physikal. Chem.*, 1903, 46, 180.
[8] Crymble, *Trans. Chem. Soc.*, 1914, 105, 658.

Reactions of Mercury Diethyl—*continued.*

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Mercuric chloride.	Heat with rather less than calculated quantity of $HgCl_2$ or alcoholic solution.	Ethyl mercuric chloride.	Frankland, *Annalen*, 1859, 111, 60; *Jahresber.*, 1859, p. 413; Frankland and Duppa, *Trans. Chem. Soc.*, 1863, 16, 415; *Annalen*, 1864, 130, 104.
Phosphorus trichloride.	Heat.	Ethyl dichlorophosphine, $EtPCl_2$.	Guichard, *Ber.*, 1899, 32, 74; see Michaelis, *Ber.*, 1880, 13. 2174.
Arsenic trichloride.	Excess of trichloride.	Ethyl dichloroarsine.	La Coste, *Annalen*, 1881, 208, 33.
Antimony trichloride.	..	Ethyl mercuric chloride. triethylstibine.	Buckton, *Trans. Chem. Soc.*. 1863. 16. 22; *Jahresber.*. 1863, p. 470.
Potassium permanganate.	Boil mixture in aqueous solution.	Ethyl mercuric hydroxide.	Seidel, *J. prakt. Chem.*, 1884. (2). 29, 134.
	Heat.	Mercury, combustible gas.	Buckton, *loc. cit.*
Iodoform.	Heat to 90° C.	Acetylene, ethylene, ethyl mercuric iodide, ethyl iodide.	Suida, *Monatsh.*, 1880, 1, 716.
Allyl iodide.	Heat at 120–150° C.	Diallyl, ethyl mercuric iodide, ethyl iodide.	do.
Phenyl iododichloride.	..	Iodobenzene, ethyl chloride, ethyl mercuric chloride.	Willgerodt, *Ber.*, 1897, 30, 57; 1898, 31, 921.
Phenylarsenious sulphide.	Heat.	Phenyl diethyl arsine, mercuric sulphide.	Michaelis and Schulte, *Ber.*, 1882, 15, 1956.
Arsenobenzene.	Heat to 150° C.	Phenyl diethyl arsine, metallic mercury.	Michaelis and Schulte, *loc. cit.*; *Ber.*, 1881, 14, 1952.
Sodium.	Heat to 100–170° C.	Sodium ethyl. Equal volumes of ethane and ethylene.	Schorigin, *Ber.*, 1910, 43, 1931; *cf.* Buckton, *Annalen*, 1859, 112, 220.
Sodium and carbon dioxide.	Substances heated in ether solution and gas passed in.	Propionic acid (sodium salt).	Schorigin, *Ber.*, 1908, 41, 2722.
Sodium and benzophenone.	Ether solution in hydrogen or nitrogen atmosphere.	Ethyldiphenylcarbinol.	do.
Sodium and methyl ester of benzoic acid.	Do.	Diethylphenylcarbinol.	do.
Sodium and benzaldehyde.	..	Ethylphenylcarbinol.	do.

DropBooks

Reactions of Mercury Diethyl—*continued.*

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Magnesium.	Heat at 130° C. for 36 hours.	Magnesium diethyl. mercury.	Löhr, *Annalen*, 1891, **261**, 4 Fleck, *Annalen*. 1893, **276**, 12
Beryllium (glucinum).	Heat at 135° C. in sealed tube.	Beryllium diethyl.	Cahours, *Compt. rend.*, 1873, 7 1383; *Jahresber.*, 1873, 520.
Cadmium.	Heat at 100–130° C.	Cadmium diethyl (not free from mercury).	Frankland and Duppa, *Tran Chem. Soc.*, 1864, 17, 2 *Annalen*. 1864, 130. 117.
Zinc.	Heat at 100° C. for 36 hours.	Zinc diethyl. mercury.	do.
Copper.	Heat at 150° C. for 5–6 hours.	Slight amalgamation and a gas evolved.	do.
Aluminium.	..	Aluminium triethyl.	Cahours, *Annalen*. 1860, 11. 242; Buckton and Odling *Annalen Suppl.*, 1866. 109–11 *Proc. Roy. Soc.*, 1865, 14, 19.
Iron (reduced from sesquioxide by hydrogen).	..	Metallic mercury, no trace of organic compound.	Frankland and Duppa, *loc. cit.*
Bismuth.	Heat at 120–140° C.	Bismuth triethyl.	do.
Silver, gold, zirconium.	Heat at 150° C.	No organic compounds.	do.
Tellurium.	..	Tellurium diethyl.	Zeiser, *Ber.*, 1895, 28, 1670.

Mercury di-n-propyl, $Hg(C_3H_7)_2$, may be obtained:

1. Two hundred grams of n-propyl iodide are treated with 0·2 per cent. sodium amalgam, in presence of 30 grams of methyl acetate. The resulting paste when treated with dilute potassium hydroxide, then steam distilled, yields an oil which is impure mercury dipropyl.[1]

2. By the interaction of magnesium propyl bromide and mercuric chloride or bromide.[2] 24·3 grams of mercuric bromide are added in small portions to the Grignard reagent from 23 grams of n-propyl bromide and 4·3 grams of magnesium in 100 c.c. of ether. All the mercuric bromide goes into solution and the reaction is accompanied by violent boiling, the mixture after boiling on the water-bath for one hour being decomposed by water. Extraction with ether yields 4·5 grams of mercury propyl bromide and 6·0 grams of mercury dipropyl, B.pt. 189° to 191° C. A small quantity of metallic mercury is also obtained.

[1] Cahours, *Compt. rend.*, 1873, 76, 135; *Jahresber.*, 1873, p. 517; Schtscherbakow, *J. Russ. Phys. Chem. Soc.*, 1881, 13, 353; *Chem. Zentr.*, 1881, 620; Goret, *Bull. Soc. Pharmacol.*, 1922, 29, 297; *Chem. Zentr.*, 1922, (iii.), 1371.

[2] Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153; Goddard, *Trans. Chem. Soc.*, 1923, 123, 1168.

Mercury di-n-propyl is a liquid having a faint odour which becomes very penetrating when heated, B.pt. 189° to 191° C., 75° to 77° C. at 25 mm. It is insoluble in water, more readily in alcohol, and very soluble in ether. At 16° C. its density is 2·124, and at 0° C. 2·046.[1]

1. When the compound is distilled it undergoes partial decomposition and mercury separates out.[2]

2. It reacts with iodine very vigorously, forming propyl iodide and propyl mercuric iodide, but with 2 mols. of iodine, propyl iodide and mercuric iodide, whilst bromine water yields brilliant laminæ of propyl mercuric bromide.[3]

3. When boiled with acids, propane is evolved and propyl mercuric salts formed.[3]

4. With tin tripropyl iodide it yields tin tetrapropyl.[3]

5. Zinc decomposes mercury dipropyl at 100° to 120° C. with the formation of zinc dipropyl; aluminium at 130° C. yields aluminium tripropyl, and beryllium gives beryllium dipropyl.

6. When treated with thallic chloride, propyl mercuric chloride, thallous chloride, and thallium dipropyl chloride are obtained.[4]

Mercury di-isopropyl, B.pt. 119° to 121° C. at 125 mm.;[5] n_D 1·532.

Mercury di-n-butyl, B.pt. 120° to 123° at 23 mm. Yield 47 per cent.

Mercury di-isobutyl may be prepared as follows :—

Fifty grams of isobutyl iodide and 10 grams of ethyl acetate are shaken with a considerable excess of 0·25 per cent. sodium amalgam. After completion of the reaction the whole is treated with water and ether, the ether layer extracting the mercury dialkyl and di-isobutyl, the latter being removed by distillation in steam. Again take up in ether, and dry the ethereal solution over calcium and fractionally distil, when mercury di-isobutyl distils at 140° C. at 70 mm.[6] Mercury di-isobutyl is a liquid having a feeble odour when cold, but becoming penetrating when hot. It is volatile in steam and boils at 205° to 207° C.; density at 15° C., 1·835; at 16° C., 1·719; at 0° C., 1·747.[7] When treated with halogens it yields isobutyl halides and isobutyl mercuric halides. By heating at 150° C. with metallic zinc for thirty-six hours, and fractionating the resulting product in hydrogen, zinc di-isobutyl is obtained, whilst aluminium at 120° to 125° C. reacts rapidly with the mercury compound to yield aluminium tri-isobutyl.

Mercury di-sec-butyl is obtained as follows :—

1. This compound is obtained in good yield when methyl ethyl ketone is electrolysed, using a mercury cathode. The best yields are produced at temperatures between 45° and 50° C., using a current of 25 amperes per square decimetre and a voltage of 7·6 to 8·4. The cathode liquid consists of the ketone with about thirteen times its weight of 30 per cent. sulphuric acid, the anode liquid being 20 per cent.

[1] Cahours, *Compt. rend.*, 1873, 76, 749.
[2] Schtscherbakow, *loc. cit.*
[3] Cahours, *loc. cit.*
[4] Goddard, *loc. cit.*
[5] Marvel and Gould, *loc. cit.*; see Tafel, *Ber.*, 1906, 39, 3626.
[6] Marquardt, *Ber.*, 1888, 21, 2035; Cahours, *Compt. rend.*, 1873, 77, 1405; *J. prakt. Chem.*, 1873, [2], 8, 397; Chapman and Smith, *Trans. Chem. Soc.*, 1869, 22, 163; Ponzio, *Gazzetta*, 1900, 30, (ii.), 24; Ssokolow, *J. Russ. Phys. Chem. Soc.*, 1887, 19, 202.
[7] See Louise and Roux, *Compt. rend.*, 1888, 107, 601.

sulphuric acid. In two hours the amount of crude mercury dialkyl is 1·3 times the weight of ketone used, and the product is then distilled in a high vacuum to purify it.[1]

2. The solution from 12 grams of magnesium, 75 grams of sec-butyl bromide in 500 c.c. ether, is treated with 45 grams of mercuric chloride, and the mixture then boiled for eight hours on the water-bath and decomposed in the usual way. Yield 66 per cent.[2]

Mercury di-sec-butyl is a colourless oil, B.pt. 46° C. at 0·3 mm., 91° to 93° C. at 15 mm., 93° to 96° C. at 18 mm.; density 1·763 at 20° C.; n_D 1·511 at 20° C. It cannot be distilled under ordinary pressures without decomposition, and when its ether solution is treated with iodine, sec-butyl iodide and sec-butyl mercuric iodide are formed.

Mercury di-tert-butyl is prepared in the manner described above. A considerable amount of tert-butyl mercuric bromide is produced during the reaction. The yield of the mercury dialkyl is only 9 per cent., B.pt. 78° to 82° C. at 5 mm., and even at this low pressure a large amount of the substance is decomposed, even the final product containing some hydrocarbon. Density 1·749 at 20° C.; n_D 1·521.

Mercury di-isoamyl.—This compound may be prepared in the same way as mercury di-isobutyl by replacing the isobutyl iodide by isoamyl iodide. It is a colourless, transparent, mobile liquid, possessing a faint amyl odour, and cannot be distilled even *in vacuo* without partial decomposition, although it is volatile in steam without decomposition. If heated above 140° C. considerable quantities of mercury separate. Its boiling-point at 70 mm. is 172° C., and the density at 0° C. is 1·6663.[3]

Mercury di-isoamyl is insoluble in water, slightly in alcohol, but readily soluble in ether. It does not oxidise in air, but when dropped into chlorine it forms isoamyl mercuric chloride. In contact with solid iodine it reacts with a hissing sound, and the reaction with bromine is still more violent. An ethereal solution of mercury di-isoamyl treated first with alcoholic and then with solid iodine gives isoamyl mercuric iodide and isoamyl iodide. Treatment with an excess of mercuric chloride in alcohol yields isoamyl mercuric chloride.

With sodium, sodium isoamyl is formed, but in ethereal solution in a stream of carbon dioxide, isobutyl acetic acid results.[4] Mercury di-isoamyl heated with zinc in a sealed tube for thirty-six hours at 130° C. yields zinc di-isoamyl.[5] The mercury compound and glacial acetic acid heated for sixteen hours at 200° C. give isopentane, metallic mercury, and amyl acetate.[6] Treatment with thallic chloride gives isoamyl mercuric chloride and thallous chloride.[7]

Mercury di-tert-amyl.—To the solution from 12 grams of magnesium and 80 grams of tert-amyl bromide in 500 c.c. of ether, 40 grams of mercuric bromide are added and the product worked up in the usual way. Yield 9 grams (21 per cent.). The liquid boils at 80°

[1] Tafel, *Ber.*, 1906, 39, 3626.
[2] Marvel and Calvery, *J. Amer. Chem. Soc.*, 1923, 45, 820.
[3] Frankland and Duppa, *Trans. Chem. Soc.*, 1863, 16, 415; *Annalen*, 1864, 130, 104; Marquardt, *Ber.*, 1888, 21, 2035.
[4] Schorigin, *Ber.*, 1908, 41, 2722; 1910, 43, 1937.
[5] Frankland and Duppa, *Trans. Chem. Soc.*, 1864, 17, 29; *Annalen*, 1864, 130, 117.
[6] Jones and Werner, *J. Amer. Chem. Soc.*, 1918, 40, 1257.
[7] Goddard, *Trans. Chem. Soc.*, 1923, 123, 1168.

to 84° C. at 5 mm., and even under these conditions shows considerable decomposition. Density 1·649 at 20° C.; n_D 1·492 at 20° C.[1]

Mercury di-n-heptyl[2] is prepared in 90 per cent. yield by the Grignard reaction. It distils at 119° to 122° C.; density 1·474 at 0° C.; n_D 1·4935 at 21° C.

Mercury di-n-octyl.[3]—Octyl iodide is treated with dilute sodium amalgam in the presence of ethyl acetate, and after completion of the reaction the mass is extracted with ether. Evaporation of the solvent gives an oily liquid of density 1·342 at 17° C., which decomposes at about 200° C. into di-octyl and metallic mercury. When the starting materials are pure it is stated that no by-products occur. Mercury di-n-octyl is insoluble in water, but readily soluble in alcohol, ether, or benzene. Treatment with alcoholic iodine or mercuric chloride yields the corresponding di-n-octyl mercuric halides.

Mercury di-sec-octyl.[4]—To the solution from 8 grams of magnesium and 70 grams of sec-octyl bromide (2-bromo-octane) in 500 c.c. of ether, 21 grams of mercuric chloride are added, and after boiling for six hours the product is worked up in the usual way. It is found to be impossible to distil the compound under 3 mm. pressure, owing to its ease of decomposition with the formation of mercury. The weight of crude product is about 48 grams (52 per cent.); density 1·338 at 20° C.; n_D 1·334 at 20° C.

Alkyl Compounds of the Type RHgX.

The following salts of the methyl series have been prepared:—

Methyl mercuric hydroxide has recently been obtained in the free state, and its solution may be obtained by boiling mercury dimethyl with concentrated potassium permanganate and filtering off the manganese dioxide, the filtrate being strongly basic and yielding salts with acids.[5] A similar solution is also obtained when methyl mercuric iodide is treated with water and silver oxide.[6] If the silver oxide be replaced by potassium hydroxide, Frankland states that the oxide is obtained which is soluble in excess of the reagent. The solid hydroxide is formed when moist silver oxide reacts with methyl mercuric iodide in methyl alcohol. It melts at 95° C., is a weak base, acid to phenolphthalein but alkaline to litmus.[7]

The *chloride*, M.pt. 170° C., forms pearly plates, density 4·063,[8] which are volatile in steam. It has been prepared in several ways:

1. By the action of concentrated hydrochloric acid or phosphorus trichloride on mercury dimethyl.[9]

2. By the addition of hydrochloric acid to the solution of methyl mercuric hydroxide described above.

3. From the compound of stannous chloride and mercury dimethyl by treatment with water.[9]

[1] Marvel and Calvery, *J. Amer. Chem. Soc.*, 1923, 45, 822.
[2] Hager and Marvel, *J. Amer. Chem. Soc.*, 1926, 48, 2696.
[3] Eichler, *Ber.*, 1879, 12, 1879.
[4] Marvel and Calvery, *loc. cit.*
[5] Seidel, *J. prakt. Chem.*, 1884, [2], 29, 134.
[6] Frankland, *Annalen*, 1853, 85, 361.
[7] Sneed and Maynard, *J. Amer. Chem. Soc.*, 1922, 44, 2942.
[8] Schröeder, *Ber.*, 1879, 12, 563.
[9] Buckton, *Annalen*, 1858, 108, 103; *Jahresber.*, 1858, p. 388.

4. 25 grams of mercuric chloride are dissolved in 10 per cent. hydrochloric acid and shaken with 15 grams of aluminium carbide, when heat is evolved and the methyl mercuric chloride is distilled out in steam.[1] (Yield 30 per cent.)

Crymble [2] has shown that compounds of the base MeHg- arranged in order of increasing absorptive power are as follows: MeHgOH, —Cl, —Br, —I, the absorption of the alkyl haloid always being less than that of the corresponding dihaloid compound.[3] The conductivity of the chloride in liquid ammonia has been investigated by Franklin,[4] and the molecular weight determined in methyl or ethyl sulphide solution has been shown to be normal.[5]

The *bromide* was used by Crymble in his investigations on absorption spectra, and the melting-point was stated to be 160° C. It can be prepared in the same way as the chloride.

The *iodide* was discovered in 1852 by Frankland,[6] who showed that methyl iodide and metallic mercury when exposed to sunlight or diffused daylight combine to form mercury methyl iodide. Other methods of preparation are:

1. Treatment of mercury dimethyl with iodine or mercuric iodide.[7]
2. By treating the chloride in aqueous solution with potassium iodide.[8]
3. From magnesium methyl iodide by treatment with an excess of mercuric chloride. Yield 85 to 88 per cent.[9]
4. Dimercurimethylene iodide is treated with aqueous potassium iodide or dilute hydrochloric acid.[10]

The compound crystallises in pearly plates, M.pt. 143° C., insoluble in water, fairly soluble in alcohol, easily in methyl iodide and ether. It sublimes without decomposition and yields the oxide with alkalies or ammonium hydroxide, whilst ammonium sulphide precipitates the sulphide in faint yellowish flocks.[11] Distillation with potassium cyanide, potassium hydroxide, or metallic potassium gives mercury dimethyl. Its molecular weight in methyl or ethyl sulphide is normal.[12]

The *bicarbonate* is formed by passing carbon dioxide through a methyl alcoholic solution of the hydroxide. It is a granular powder, M.pt. 123° C. When dissolved in carbon disulphide it yields the mercaptan, silvery plates, M.pt. 143° C., MeHgSH.[13]

The *nitrate* forms colourless plates, M.pt. 100° C., and may be prepared from the iodide by treatment with silver nitrate.[14] It is very soluble in water, less soluble in alcohol.

The *sulphate* is a crystalline compound obtained by the action of concentrated sulphuric acid on mercury dimethyl.[15]

[1] Hilpert and Ditmar, *Ber.*, 1913, 46, 3738.
[2] Crymble, *Trans. Chem. Soc.*, 1914, 105, 658.
[3] *Cf.* Ley and Fischer, *Zeitsch. anorg. Chem.*, 1913, 82, 338.
[4] Franklin, *Zeitsch. physikal. Chem.*, 1909, 69, 299.
[5] Werner, *Zeitsch. anorg. Chem.*, 1897, 15, 37.
[6] Frankland, *Annalen*, 1853, 85, 363; *Jahresber.*, 1852, p. 574.
[7] Buckton, *Annalen*, 1858, 108, 103; *Jahresber.*, 1858, p. 388.
[8] Hilpert and Ditmar, *loc. cit.*
[9] Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153.
[10] Sakural, *Trans. Chem. Soc.*, 1881, 39, 485.
[11] Frankland, *loc. cit.*
[12] Werner, *loc. cit.*
[13] Koten and Adams, *J. Amer. Chem. Soc.*, 1924, 46, 2768.
[14] Strecker, *Annalen*, 1854, 92, 79.
[15] Buckton, *loc. cit.*

Acetate.—This compound was first obtained by heating mercury dimethyl and glacial acetic acid in a sealed tube for one hour, then recrystallising the product from glacial acetic acid.[1] The melting-point given was 142° to 143° C., but recently Sneed and Maynard[2] have shown this to be inaccurate, and obtained the product by the following methods, each giving a substance M.pt. 128° C.: (1) Treatment of mercury dimethyl in methyl alcohol solution with mercuric acetate. (2) Neutralisation of the hydroxide with glacial acetic acid. (3) Action of silver acetate on the iodide. (4) Action of ethyl acetate on the hydroxide. The acetate is very soluble in water, alcohol, or acetic acid, is volatile in steam, and with concentrated hydrochloric acid or iodine yields the corresponding halides.

Sulphide.—This substance may be obtained from the iodide as stated above or by the action of hydrogen sulphide on a solution of the chloride.[3] It is a white body of characteristic smell, and when warmed it decomposes, forming mercury dimethyl and splitting off mercuric sulphide.

Ethyl Series.—*Hydroxide.*—A solution of this compound may be prepared by boiling mercury diethyl with potassium permanganate solution, see methyl mercuric hydroxide.[4] Dünhaupt[5] obtained the hydroxide as a colourless oil by boiling ethyl mercuric chloride in spirit with silver oxide, filtering off the silver chloride, then distilling off the spirit and drying the product *in vacuo* over sulphuric acid. It is easily soluble in water or spirit and has all the properties of a strong base. With ammonium chloride it liberates ammonia and forms the chloride of the base, and with solutions of salts of copper, aluminium, iron, tin, gold, or platinum it precipitates hydroxides. With metallic zinc it forms zinc amalgam and zinc diethyl, whilst hydrogen sulphide gives a white precipitate which soon turns yellow and finally black. When treated with acids the hydroxide yields salts in the usual way; with alkaline stannous chloride solution it is reduced to mercury diethyl and mercury.[6]

The *chloride* may be obtained: (1) From the hydroxide by hydrochloric acid or ammonium chloride. (2) By mixing a warm alcoholic solution containing one molecular proportion of mercuric chloride with mercury diethyl.[7] (3) By the action of concentrated hydrochloric acid or antimony trichloride on mercury diethyl.[8] (4) From mercury diethyl and phenyl iododichloride.[9]

The chloride crystallises in silver glistening plates, M.pt. 190° to 193° C., density 3·482, which sublime on gentle warming and are easily soluble in boiling alcohol, with difficulty in ether, and insoluble in water.[10]

Bromide.—This compound has similar properties to the above chloride, and may be prepared from the hydroxide by the addition of hydrobromic acid, by treating an alcoholic solution of mercuric bromide with triethyl bismuthine or by heating mercury diethyl and ethyl

[1] Otto, *Annalen*, 1870, 154, 198.
[2] Sneed and Maynard, *J. Amer. Chem. Soc.*, 1922, 44, 2942.
[3] Hilpert and Ditmar, *Ber.*, 1913, 46, 3738.
[4] Seidel, *J. prakt. Chem.*, 1884, [2], 29, 134.
[5] Dünhaupt, *J. prakt. Chem.*, 1854, [1], 61, 399; *Annalen*, 1854, 92, 379.
[6] Dimroth, *Chem. Zentr.*, 1901, i. 451; *Ber.*, 1902, 35, 2853.
[7] Frankland, *Annalen*, 1859, 111, 60; *Jahresber.*, 1859, p. 413.
[8] Buckton, *Annalen*, 1859, 109, 220; *Jahresber.*, 1858, p. 390; *Trans. Chem. Soc.*, 1863, 16, 22; *Jahresber.*, 1863, p. 470.
[9] Willgerodt, *Ber.*, 1898, 31, 921.
[10] Dünhaupt, *J. prakt. Chem.*, 1854, [1], 61, 399; *Annalen*, 1854, 92, 379; Schröder, *Ber.*, 1879, 12, 563.

monobromoacetate at 150° C. for eight hours. The reaction in the latter case takes place according to the equation :

$$CH_2Br.COOC_2H_5 + (C_2H_5)_2Hg = C_2H_5HgBr + CH_3COOC_2H_5 + CH_4$$ [1]

The bromide crystallises in pearly plates, M.pt. 193·5° C.[2]

Iodide.—Combination takes place between ethyl iodide and metallic mercury when exposed to diffused daylight, with formation of ethyl mercuric iodide.[3] This may also be obtained by the addition of an alcoholic solution of iodine to ethyl mercuric hydroxide,[4] or from mercury diethyl by boiling for one or two days with allyl iodide. Another preparation from mercury diethyl is to heat for several days at 120° C. with iodoform, when the iodide, ethyl iodide, ethylene, and acetylene are formed.[5]

The iodide, M.pt. 182° C., crystallises from ether-alcohol solution in colourless plates which have a very pungent odour. It sublimes without decomposition at 100° C., is soluble with difficulty in water, and is decomposed by light.

Sulphide.—When ammonium sulphide is added to an alcoholic solution of ethyl mercuric chloride, a yellow precipitate is thrown down which is soluble in excess of the reagent. It may be recrystallised from ether, but evaporation of the alcoholic solution soon leads to decomposition of the compound.

Mercaptan, Et.HgSH.—By dissolving the bicarbonate in carbon disulphide, silvery plates, M.pt. 104° C.,[6] of the mercaptan are obtained.

The *sulphate* crystallises in glistening plates, when silver sulphate is added to ethyl mercuric chloride in alcohol. It is also formed when concentrated sulphuric acid reacts with mercury diethyl.[7]

The *nitrate* was only obtained by Dünhaupt as an oil, but Strecker succeeded in isolating it in prisms which were very soluble in alcohol, but less soluble in water.

The *acetate,* M.pt. 178° C., has similar properties to the corresponding methyl compound and may be prepared in similar manner.[8]

The 2.4.6-*trinitrobenzoate* is formed by treating the substituted benzoic acid in alcohol with a similar solution of ethyl mercuric hydroxide. It forms white plates, M.pt. 164° C. When heated at 165° C. it yields ethylmercuric 2.4.6-trinitrophenyl, yellow needles, M.pt. 86° C.[9] Dünhaupt, by treatment of ethyl mercuric chloride with silver phosphate, isolated the *phosphate* as a crystalline mass very soluble in water, also he mentions a *cyanide* which is crystalline, very volatile, and of repulsive odour.

The *thiocyanate* is formed from the chloride by the action of sodium thiocyanate (1 mol.) in acetone solution. It crystallises from benzene in glistening plates, M.pt. 131° to 131·5° C.[10]

[1] Dünhaupt, *J. prakt. Chem.*, 1854, [1], 61, 399; *Annalen*, 1854, 92, 379; Sell and Lippmann, *J. prakt. Chem.*, 1866, [1], 99, 431; Buckton, *Annalen*, 1859, 112, 221.
[2] Marvel, Gauerke, and Hill, *J. Amer. Chem. Soc.*, 1925, 47, 3009.
[3] Frankland, *Annalen*, 1859, 111, 59; Strecker, *Annalen*, 1854, 92, 76.
[4] Dünhaupt, *loc. cit.*
[5] Suida, *Monatsh.*, 1880, i. 715; *Jahresber.*, 1881, p. 940.
[6] Koten and Adams, *J. Amer. Chem. Soc.*, 1924, 46, 2768.
[7] Buckton, *Annalen*, 1858, 109, 220; 1859, 112, 221; *Jahresber.*, 1858, p. 390; 1859, p. 408; *J. prakt. Chem.*, 1860, 1, 79; Schorlemmer, *Annalen*, 1864, 132, 234.
[8] Otto, *Annalen*, 1870, 154, 198.
[9] Koten and Adams, *loc. cit.*
[10] Steinkopf, *Annalen*, 1921, 424, 59.

n-Propyl Series.[1]—*n-Propyl mercuric hydroxide* is difficult to obtain in a crystalline condition; it is a strong base, forming salts with strong and weak acids.

The *chloride* may be formed from the base, by boiling mercury dipropyl with hydrochloric acid or by the addition of mercuric chloride to mercury dipropyl in alcoholic solution. It crystallises in white scales, M.pt. 143° C.

When bromine or bromine water is added to mercury dipropyl, or the base is treated with hydrobromic acid, *propyl mercuric bromide* is obtained in leaflets, M.pt. 138° C. The compound is also formed as a by-product in the preparation of mercury dipropyl from propyl magnesium bromide and mercuric bromide.[2]

Iodine combines vigorously with mercury dipropyl to form the *iodide*, M.pt. 113° C.; this crystallises from alcohol in plates which have a disagreeable odour.

The *acetate* from mercury dipropyl and acetic anhydride, or acetic acid and the corresponding hydroxide, is crystalline, M.pt. 57° to 58° C.

Isopropyl Series.[3]—*iso-propyl mercuric hydroxide* is formed by treating the halides with moist silver oxide, and has only been obtained in solution. It reacts with acids, giving rise to the following compounds: *chloride*, needles, M.pt. 97° C.; *bromide*, needles, M.pt. 98° C.; *iodide*, plates, M.pt. 125° C.; *acetate*, M.pt. 95° C.; *cyanide*, M.pt. 85° C.; *sulphide*, M.pt. 60° C.

n-Butyl Series.—When n-butyl magnesium bromide is treated with an excess of mercuric chloride, a mixture of equal parts of *n-butyl mercuric chloride* and *bromide* are formed.[4] The chloride melts at 127·5° C.; the bromide at 129° C.; the *iodide* at 117° C.[5]

iso-Butyl Series.—Solutions of *isobutyl mercuric hydroxide* may be obtained in the usual way, and salts prepared by the addition of acids. Mercury di-isobutyl reacts with iodine, giving a crystalline *isobutyl mercuric iodide*.[6] The *bromide* melts at 55·5° C. and the iodide at 72° C.[7]

sec-Butyl Series.—When mercury di-sec-butyl is dissolved in alcohol and treated with aqueous hydrochloric acid the *sec-butyl mercuric chloride* separates out as an oil. This may be solidified by cooling in a freezing mixture. The crystals obtained melt at 30·5° C.[8]

The *bromide* is prepared as above using hydrobromic acid, and melts at 39° C. The *iodide* forms colourless, unstable crystals when the dialkyl is treated with iodine.[9]

tert-Butyl Series.—*tert-Butyl mercuric bromide.*—An excess of mercuric bromide is added to well-cooled Grignard reagent from tert-butyl bromide and after an hour the whole decomposed with water, the ether layer removed and dried over calcium chloride. Spontaneous evaporation of the ether gives a product, M.pt. 106° C. (decomp.). It is rapidly decomposed in bright sunlight.[10]

[1] Cahours, *Compt. rend.*, 1873, 76, 135, 749, 750; *Jahresber.*, 1873, p. 517; Goret, *Bull. Sci. Pharmacol.*, 1922, 29, 297; *Chem. Zentr.*, 1922, iii. 1371.
[2] Goddard, *Trans. Chem. Soc.*, 1923, 123, 1168.
[3] Goret, *loc. cit.*
[4] Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153.
[5] Marvel, Gauerke, and Hill, *loc. cit.*
[6] Cahours, *Compt. rend.*, 1873, 76, 1403.
[7] Marvel, Gauerke, and Hill, *loc. cit.*
[8] Marvel and Calvery, *J. Amer. Chem. Soc.*, 1923, 45, 821.
[9] Tafel, *Ber.*, 1906, 39, 3631.
[10] Marvel and Calvery, *loc. cit.*

n-Amyl Series.—*n-Amyl mercuric bromide*, obtained in the usual way, melts at 122° C.[1]

iso-Amyl Series.—*Isoamyl mercuric chloride*[2] is formed when mercury di-isoamyl is treated with chlorine gas or alcoholic mercuric chloride. It melts at 86° C., sublimes without decomposition, and is very soluble in ether or hot alcohol, insoluble in water. From alcohol it crystallises in hair-like needles. The *bromide* melts at 80° C. When an ethereal solution of mercury di-isoamyl is treated first with alcoholic iodine, then with solid iodine, it yields isoamyl iodide and *isoamyl mercuric iodide*. The latter recrystallises from hot alcohol in small pearly plates, M.pt. 122° C., very soluble in ether, slightly soluble in boiling water, insoluble in cold water, and partially decomposed by alcoholic potassium hydroxide. In the molten state it turns yellow at 140° C., owing to the separation of mercuric iodide. It may be sublimed without decomposition in a current of air.[3]

tert-Amyl Series.—*tert-Amyl mercuric bromide* is prepared in the same manner as the tert-butyl compound. It crystallises from alcohol if the solution is kept below 50° C., M.pt. 82° C.[4]

Hexyl and Heptyl Series.—*n-Hexyl* and *n-heptyl mercuric bromides* melt at 118·5° C. and 114·5° C. respectively.[5]

n-Octyl Series.[6]—The *hydroxide* is formed when an alcoholic solution of the chloride is boiled for five hours with freshly precipitated silver oxide. It crystallises in shining yellow plates, M.pt. 75° C., readily soluble in cold alcohol, less soluble in hot alcohol, insoluble in cold water. The compound is a strong base and precipitates metallic salts from solutions of ferric chloride, potassium alum, zinc sulphate, or copper acetate. In the latter case the grey precipitate on warming is reduced to metallic copper, whereas with the alum, the precipitate is soluble in excess of the precipitant. The base also expels ammonia from its compounds.

The *chloride* is obtained as a white precipitate by the interaction of mercury di-n-octyl and mercuric chloride; the *iodide* by the use of iodine. The latter forms a white glistening precipitate, easily soluble in alcohol. The *bromide* melts at 109° C.[7]

sec-Octyl Series.[8]—The *bromide* is obtained from excess of mercuric bromide and the Grignard reagent from sec-octyl bromide. It forms crystals from alcohol solution, M.pt. 98° C.[9]

Allyl mercuric iodide, $CH_2=CH-CH_2-HgI$.[10]—Allyl iodide containing a trace of dissolved iodine, readily reacts with mercury. If mercury be shaken with some iodine, then with allyl iodide, an evolution of heat takes place and the mass becomes solid. This may be avoided to some extent by mixing the allyl iodide with alcohol. The iodide crystallises from alcohol in silvery scales, which turn yellow on drying. It commences to volatilise at 100° C. and melts at 135° C.,

[1] Marvel, Gauerke, and Hill, *J. Amer. Chem. Soc.*, 1925, 47, 3009.
[2] Marvel and Calvery, *J. Amer. Chem. Soc.*, 1923, 45, 821.
[3] Frankland and Duppa, *Trans. Chem. Soc.*, 1863, 16, 415; *Annalen*, 1864, 130, 104.
[4] Marvel and Calvery, *loc. cit.*
[5] Marvel, Gauerke, and Hill, *loc. cit.*
[6] Eichler, *Ber.*, 1879, 12, 1879.
[7] Marvel, Gauerke, and Hill, *loc. cit.*
[8] Eichler, *loc. cit.*
[9] Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153.
[10] Zinin, *Annalen*, 1855, 96, 363; Linnemann, *Annalen Suppl.*, 1865, 3, 262; *Annalen*, 1866, 140, 180.

decomposing at higher temperatures with evolution of gas and formation of a yellowish-red residue. The iodide is sparingly soluble in cold alcohol and insoluble in water. When subjected to dry distillation, diallyl, metallic mercury, and mercuric iodide are formed. Hydrogen sulphide or iodide decompose it, propylene and mercuric salts being obtained. Iodine yields allyl iodide and mercuric iodide. Alcoholic suspensions of silver oxide convert the iodide to the *hydroxide*.

Propargyl mercuric iodide forms a yellow mass; it is prepared in a similar way to the allyl compound.[1]

Mercury Derivatives of Methylene Iodide.—Wanklyn and Von Than [2] showed that neither mercury nor zinc gave organic compounds when allowed to react with ethylene iodide.

Methylene iodide, on the other hand, when left in contact with metallic mercury and some mercurous iodide in a sealed tube for four or five days, combines with the mercury.[3] Two products are produced, but no gas is evolved when the tube is opened. The first compound crystallises from boiling alcohol in slender, white needles; it is best purified by solution in methylene iodide and precipitation with ether, and is insoluble in the usual solvents. Sakurai assigned the formula $I-CH_2-HgI$ to the substance. This *monomercuric methylene iodide* or *iodomethyl mercuric iodide* when heated with iodine in potassium iodide solution yields methylene iodide and mercuric iodide, and similar decomposition takes place with chlorine or bromine.

When one molecule of the compound and one molecule of mercuric chloride in alcoholic solution are boiled under reflux for one hour and then cooled, crystals are obtained from which the mercuric chloride is removed by washing with water, and the mercuric iodide by digestion with concentrated potassium iodide solution. Traces of soluble iodide are then removed by treatment with water, and the dried crystals purified by recrystallisation from ether. *Monomercuric methylene chloro-iodide*, M.pt. 129° C., is thus obtained in small plates, soluble in ether, chloroform, or alcohol, but insoluble in water.

PropBooks

$$I-CH_2-HgI+HgCl_2=Cl-CH_2-HgI+HgICl$$ [4]

The product formed along with the monomercuric methylene iodide was a white body insoluble in all the usual solvents, but yielding iodoform with iodine. Analysis points to *mercury iodoform* or *methine trimercuric iodide*, $CH(HgI)_3$, and the same compound was obtained by Hofmann [5] when an ethereal solution of iodoform was allowed to stand in contact with mercurous chloride for a long time.

Dimercuric methylene iodide or *methylene di-mercuric iodide*, $CH_2(HgI)_2$. —This compound is readily formed by the interaction of methylene iodide with excess of mercury in the presence of mercuric iodide in ether solution, the mixture merely being exposed to sunlight, the reaction taking several days for completion. The crude product is then digested with concentrated potassium iodide solution to remove mercuric iodide, and recrystallised from methylene iodide, the first product

[1] Henry, *Ber.*, 1884, **17**, 1132.
[2] Wanklyn and Von Than, *Quart. J. Chem. Soc.*, 1859, **12**, 258.
[3] Sakurai, *Trans. Chem. Soc.*, 1880, **37**, 658.
[4] Sakurai, *ibid.*, 1882, **41**, 360.
[5] Hofmann, *Ber.*, 1900, **33**, 1328.

being pure dimercuric compound, but subsequent crops of crystals contain some mono derivative.[1]

The iodide is a yellow crystalline powder, M.pt. 230° C., with decomposition, and is much less soluble than the mono compound in methylene iodide, and is insoluble in ordinary solvents. When treated with iodine it yields mercuric iodide and methylene iodide; and with aqueous potassium iodide or dilute hydrochloric acid, methyl mercuric iodide is formed.

[1] Sakurai. *Trans. Chem. Soc.*, 1881, 39, 485.

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CHAPTER IV.

MERCURY (*continued*).

Derivatives of Aliphatic Alcohols, Aldehydes, and Ketones.

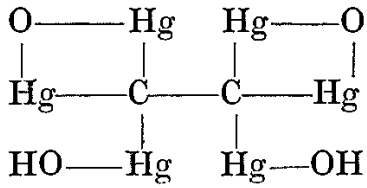
The earliest recorded work on the mercuration of alcohols was that of Sobero and Selmi,[1] and Gerhardt,[2] but none of these investigators obtained any definite results. Reynoso, five years later,[3] described compounds which he did not even analyse, and Cowper,[4] from his work on the interaction of mercuric nitrate and alcohol, added nothing to our knowledge of these compounds. Tertiary alcohols were investigated by Denigès,[5] who treated these compounds with mercuric nitrate or sulphate and obtained orange and yellow insoluble compounds respectively. He never seemed very certain of the constitutions of any of his derivatives, but recommended that his reactions might be used as tests for tertiary alcohols.

In 1898, K. A. Hofmann commenced his researches on the mercuration of alcohol, which led to the complex compounds to which he gave the name mercarbides being isolated. These compounds have all the hydrogen of a methyl group replaced by mercury. From this time onwards it has been possible to assign formulæ to most of the compounds described.

DropBooks

Derivatives of Ethyl Alcohol.

Ethane hexamercarbide, $C_2Hg_6O_2(OH)_2$, or

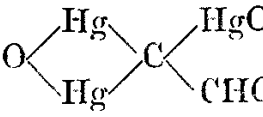


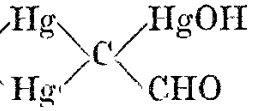
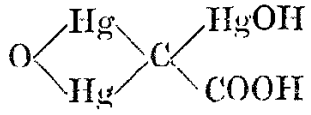
This compound is the ultimate product from the prolonged action of yellow mercuric oxide and boiling aqueous alkali on ethyl, propyl, allyl, or amyl alcohols, acetaldehyde, cellulose, starch, or cane sugar; but it cannot be obtained from methyl alcohol, formaldehyde, or glycerol. The preparation is best carried out as follows: 100 grams of yellow mercuric oxide, 20 grams of potassium hydroxide, and 200 grams of 94 per cent. ethyl alcohol are boiled for thirty-six hours, the grey residue then washed with water and dilute alkali, and finally with hot 20 per cent. nitric acid. The latter changes the base into the nitrate and removes

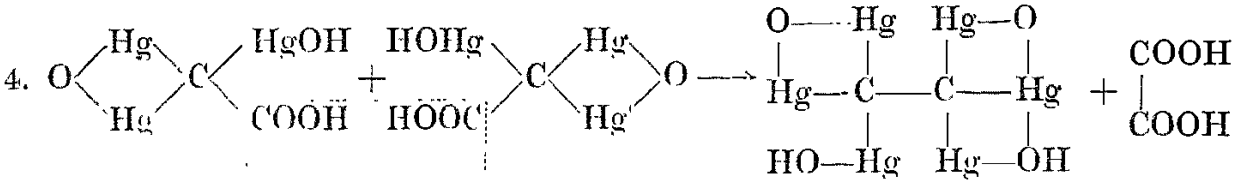
[1] Sobero and Selmi, *Annalen*, 1851, 80, 108.
[2] Gerhardt, *Annalen*, 1851, 80, 111.
[3] Reynoso, *Ann. Chim. Phys.*, 1856, [3], 48, 403.
[4] Cowper, *Trans. Chem. Soc.*, 1881, 39, 242.
[5] Denigès, *Compt. rend.*, 1898, 126, 1043; *Bull. Soc. chim.*, 1898, [3], 19, 494, 751; *Ann. Chim. Phys.*, 1899, [7], 18, 382.

metallic mercury and trimercuri-acetic acid, which is formed as a by-product.[1] Hofmann considered the reaction to take place in four stages, according to the following scheme :—

1. $CH_3.CH_2.OH + HgO \longrightarrow CH_3.CHO + H_2O + Hg$

2. $CH_3.CHO + 3HgO \longrightarrow$  $+ H_2O$

3.  $+ HgO \longrightarrow$  $+ Hg$

4. 

The oxalic acid shown in equation 4 was not actually isolated, however.

Ethane hexamercarbide is a citron yellow to light grey powder, becoming dark orange at 200° C. and exploding with great violence at 230° C. The colour change seems to be associated with the splitting off of water from the molecule and the formation of an anhydride ($C_2Hg_6O_2$), which is violently explosive. The mercarbide is a decided base, which shows a remarkable stability towards oxidising agents (permanganate, chromic acid, hypochlorites, and hypobromites), and even towards aqua regia provided the treatment is not too prolonged. It is scarcely attacked by sulphur dioxide, hydroxylamine, or hydrazine, but with acids it forms salts.

This resisting capacity distinguishes the compound from all known mercury derivatives, and is probably due to the protective action of the six mercury atoms, showing that they surround the two carbon atoms. Two types of salts are obtained from the base, namely: (1) $C_2Hg_6O_2X_2$, (2) $C_2Hg_6X_6$.

Class I.

Ethane hexamercarbide dichloride, $C_2Hg_6O_2Cl_2$, is formed when the base is treated with cold 10 per cent. hydrochloric acid or a soluble chloride. Similarly, using potassium bromide or iodide, the corresponding *bromide* or *iodide* is obtained.

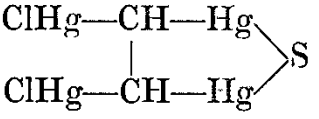
The *perchlorate*, $C_2Hg_6O_2(ClO_4)_2$, is a white powder, which on heating or rubbing explodes, emitting a green flame. The *nitrate* forms a yellowish-white crystalline mass, insoluble in water and dilute nitric acid, decomposing with explosion on heating; the *sulphate* is a white, sandy, fine crystalline powder, insoluble in water; the *picrate* explodes on heating with the same violence as potassium picrate.

Class II.

Ethane hexamercarbide hexachloride, $C_2Hg_6Cl_6$, results when the base is treated with hot hydrochloric acid. It is a white, insoluble substance,

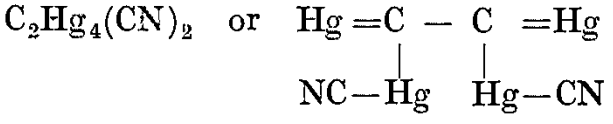
[1] Hofmann, *Ber.*, 1898, 31, 1904; 1900, 33, 1328.

which remains undecomposed when heated with ten times its weight of a 10 per cent. benzene solution of sulphur chloride. When aqueous potassium polysulphide solution is used brilliant yellow needles are deposited. These, when boiled with hydrochloric acid, yield a white powder, which becomes yellow on treatment with hot sodium hydroxide. Since chlorine atoms may be removed by means of silver nitrate, it is probable that the halogen is attached to the mercury, and the following formula has been suggested:—[1]

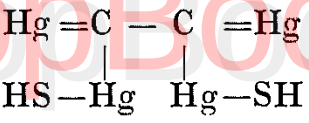


The *hexa-iodide*, $(IHg)_3C.C(HgI)_3$, is formed when the base (1 mol.) is heated with ethyl iodide (6 mols.) in ether solution for sixty hours at 90° C. The intense, reddish-yellow crystals thus obtained are very insoluble, and contain only 1·2 per cent. of carbon. This compound has the lowest carbon content of any substance yet obtained.

Whilst most carbon mercury compounds are decomposed by potassium cyanide, splitting off mercury cyanide, mercarbide *nitrate*, after prolonged boiling with potassium cyanide, splits off mercury, with the formation of an intense yellow cyanide which is explosive when heated, namely:



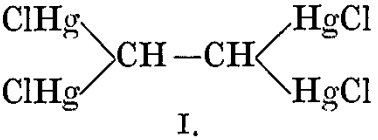
The *cyanide* is insoluble and affected by light; treatment with hydrogen sulphide transforms it into a *hydrosulphide*:



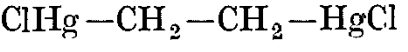
DropBooks

which is a white substance, insoluble in water, alcohol, or ether.

Hot hydrochloric acid transforms the cyanide first to a white *chloride* (I.), which by the further action of concentrated acid changes to *chloride* (II.):



I.



II.

The compound II. crystallises well from ether, and can be steam distilled, when it separates in six-sided plates, smelling strongly of potassium cyanide, M.pt. 173° C.: these crystals are soluble in water, alcohol, or ether, and are volatile and poisonous. Towards phenyl hydrazine the compound is very stable, but with potassium iodide it gives the corresponding *iodide*, $C_2H_4Hg_2I_2$, which crystallises from alcohol or ether in quadratic plates, soluble in sodium hydroxide or ammonium hydroxide, stable towards dilute acid. The hydrochloric acid solution of the iodide with hydrogen sulphide yields a white *sulphide*, crystallisable from alcohol, but insoluble in cold 20 per cent. nitric acid.

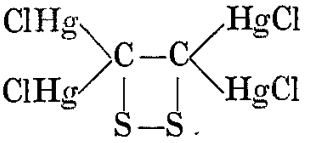
The above cyanide, whilst it yields a hydrosulphide with hydrogen sulphide, is also capable of yielding *sulphides* with potassium poly-

[1] Hofmann and Feigel, *Ber.*, 1905, 38, 3654.

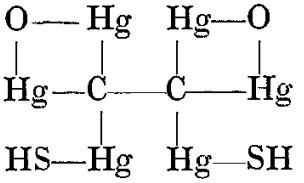
sulphide and with a methyl alcoholic solution of ammonium polysulphide, the structures of these compounds being as follows :—

$$(Hg{=}CH{-}CH_2.Hg)_2S \quad \text{and} \quad \begin{array}{c} CH_2 \text{——} CH_2 \\ | \qquad\quad | \\ Hg{-}S{-}Hg \end{array}$$

Two further sulphur compounds may be obtained from ethane hexamercarbide itself. (1) By shaking the base with a benzene solution of sulphur chloride yellow crystals are isolated, which probably have the composition :



The halogen is readily removed by silver nitrate. (2) A methyl alcoholic solution of ammonium polysulphide when left in contact with the base for several weeks yields a yellow compound, to which the following structure has been assigned :—



Ethane hexamercarbide yields a yellow substance when treated with sodium bisulphite, the product turning grey in the light ; but the base is easily regenerated by treatment first with hot nitric acid, then with sodium hydroxide.

Although the base does not combine with ammonia, its salts readily add on this gas to form stable compounds.

Hydrazine hydrate only slowly reduces the mercarbide, evolving ethane, as follows :—

$$C_2Hg_6O_2(OH)_2 + 3N_2H_4 = C_2H_6 + 6Hg + 3N_2 + 4H_2O$$

Hydrogen sulphide splits off a small quantity of mercuric sulphide, and yields a white *sulphide* of the mercarbide.

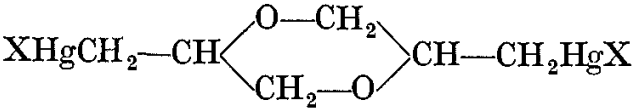
Potato starch and cane sugar also yield mercarbides,[1] of composition $C_3H_6O_2Hg_2.NO_3$ and $C_3H_6O_6Hg_4.NO_3$ respectively.

Derivatives of Allyl Alcohol.[2]

Allyl alcohol gives rise to two types of mercury compounds :

1. Propylene glycol mercuric salts, which are considered to be derivatives of the unknown γ-hydroxymercuripropylene glycol, $HOCH_2{-}CHOH{-}CH_2HgOH$.

2. Mercuridipropylene oxide salts or dipropylene oxide dimercuric salts, which have the constitution :



[1] Hofmann, *Ber.*, 1900, 33, 1333.

[2] Sand and Hofmann, *Ber.*, 1900, 33, 1358 ; Hofmann and Sand, *Ber.*, 1900, 33, 2692 ; Biilmann, *Ber.*, 1900, 33, 1641 ; 1902, 35, 2586 ; Sand, *Ber.*, 1901, 34, 1393, 2910 ; Stoehr, *J. prakt. Chem.*, 1897, [2], 55, 88.

First Type.

Propylene glycol mercuric bromide, $CH_2OH—CHOH—CH_2—HgBr$, forms white crystals from benzene-acetone solution, which melt at 84° to 86° C., and decompose at 110° C. It is easily soluble in alcohol or acetone, somewhat soluble in water, but readily decomposed by hydrochloric acid. The method of preparation is as follows : 100 grams of yellow mercuric oxide are dissolved in 20 per cent. nitric acid, and the solution treated with pure, dilute potassium hydroxide until on shaking the white precipitate of basic nitrate no longer disappears. Allyl alcohol is then added dropwise, with continuous stirring, and a clear solution is obtained; then more potassium hydroxide is added, which causes a white precipitate, the latter being dissolved by the addition of more allyl alcohol. This process is repeated, the temperature being maintained at 10° C. by cooling; the completion of the reaction is indicated by a sudden darkening of the precipitate, and the solution then has an alkaline reaction. Potassium bromide is then added, allowing one molecular weight of this salt for every atomic weight of mercury present, and after standing for twenty-four hours the bromide is precipitated by passing carbon dioxide through the mixture.

The corresponding *iodide* is prepared in a similar manner to the bromide. It may be crystallised from benzene or acetone and melts at about 80° C. It is more readily decomposed than the bromide, and hydrochloric or acetic acids break it down to allyl alcohol and mercuric salts. The presence of the two hydroxyl groups has been shown by the fact that the iodide yields a *dibenzoyl* derivative, M.pt. 100° C. When the iodide is treated with iodine at 40° C. a liquid iodohydrine is obtained.

Second Type.

Dipropylene oxide dimercuric sulphate may be prepared as follows : 75 grams of mercuric oxide are dissolved in a mixture of 300 c.c. of water and 180 c.c. of dilute sulphuric acid (1 : 1) and the solution filtered. Thirty c.c. of allyl alcohol are then stirred into the filtrate, and in two to four hours the sulphate separates out, is filtered, washed with cold water, and dried. Yield 60 grams. It gives a clear solution in water, sodium hydroxide, or ammonia, and is best purified by crystallisation from boiling water containing a little allyl alcohol, crystals containing 4 mols. of water of crystallisation being deposited. The solution in ammonium hydroxide if treated with about three volumes of alcohol yields white plates, which are an addition compound of the sulphate with 2 mols. of ammonia. This body is completely soluble in water, but gives off ammonia when boiled. The addition product with potassium bromide yields the corresponding bromide and free ammonia.

The corresponding *nitrate* crystallises with one molecule of water of crystallisation as a white crystalline compound. The preparation is similar to the sulphate, the sulphuric acid being replaced by 40 per cent. nitric acid. The product is soluble in alkali or ammonium hydroxide, and ammonium sulphide gives a yellow precipitate when added to these solutions. The aqueous solution of the nitrate has an acid reaction, and from it potassium bromide precipitates the *bromide* quantitatively. When dissolved in 20 per cent. ammonium hydroxide the nitrate gives a white crystalline body containing one molecule of ammonia, which has similar properties to the corresponding sulphate.

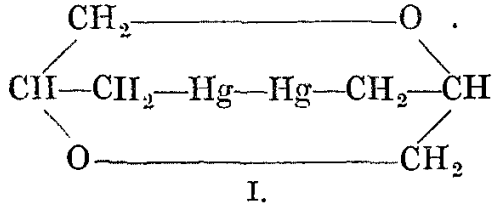
The *acetate* forms small stellate crystals when allyl alcohol is added to

a solution of mercuric oxide in dilute acetic acid. The solution in water gives precipitates with potassium chloride or bromide, but not with ammonia or alkalies. Solutions in the latter yield white precipitates with ammonium sulphide.

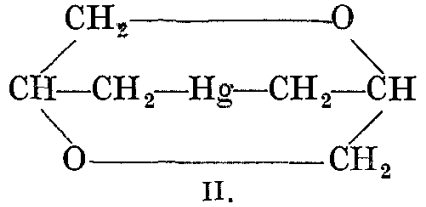
A *cyanide*, *sulphide*, and a *basic carbonate* have also been obtained from the nitrate as thick white precipitates.

The *chloride* is prepared by the action of dilute hydrochloric acid upon the nitrate, or by using potassium chloride and carbon dioxide. When treated with moist silver oxide it yields an aqueous solution of the *hydroxide*, the latter also being formed when freshly precipitated mercuric oxide, allyl alcohol, and water are shaken together. Reduction of the chloride by zinc and hydrochloric acid gives an odour of allyl alcohol, whilst oxidation with permanganate causes the immediate decomposition of the compound with the formation of oxalic acid.

The *bromide* is prepared in the same way as the chloride, is insoluble in organic solvents, and melts at 251° C. It reacts with alkaline sodium stannite solution, yielding a brick-red compound I., which turns brown on exposure to light. This decomposition product when extracted with hot benzene gives II., the corresponding mercuric compound to I. It melts at 190° C., is insoluble in water, alkalies, dilute acids, or acetone, readily soluble in benzene or toluene, and is decomposed by concentrated hydrochloric acid. With mercuric chloride or picric acid it gives precipitates, but remains unchanged when boiled with potassium hydroxide, cyanide, or iodide.

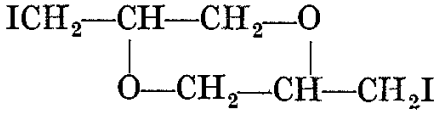


I.



II.

The *iodide* is prepared from an alkaline solution of the nitrate by the addition of potassium iodide. It may be crystallised from boiling alkali. It has M.pt. 271° C., is practically insoluble in organic solvents, and remains unchanged when treated with 20 per cent. hydrochloric acid. With iodine in potassium iodide it reacts slowly, but iodine in benzene at 140° C. gives di-*epi*-iodohydrine, to which Stoehr [1] assigns the structure :



Hofmann and Sand [2] showed the difference between the two types of compounds just discussed by the following comparisons :—

Reagent.	Propylene glycol mercuric bromide.	Dipropylene oxide di-mercuric bromide.
	$C_3H_7O_2$—HgBr. M.pt. 84–86° C.	$(C_3H_5O_2$—$HgBr)_2$. M.pt. 251° C.
Alcohol, acetone.	Easily soluble.	Insoluble.
HCl.	Rapidly decomposed.	Unattacked.
Alkaline KI.	No precipitate.	White precipitate.
,, KCN.	do.	do.
H_2S.	do.	do.

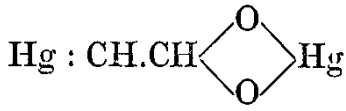
[1] Stoehr, *J. prakt. Chem.*, 1897, [2], 55, 88. [2] Hofmann and Sand, *Ber.*, 1900, 33, 2700.

Similar properties are shown by the respective iodides, whose melting-points are about 80° C. and 271° C.

Derivatives of Aldehydes.

Very little satisfactory work has been done on the mercury compounds of the aliphatic aldehydes. The chief reason for this is the fact that mercuric acetate is soon reduced by aliphatic aldehydes, paraldehyde, acetals or aldoses, mercurous acetate separating out.[1]

Leys[2] used a reagent consisting of one gram of mercuric oxide in 100 c.c. of 5 per cent. sodium sulphite solution as a test for aldehydes containing the grouping $-CH_2.CHO$. If a few drops of acetaldehyde be added to this solution in the cold and an equal volume of dilute sodium hydroxide, a heavy white precipitate is obtained, to which Leys assigned the formula:

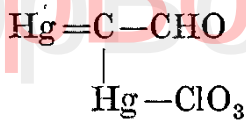


The author stated that the only substances which yielded precipitates with the reagent were terpenes, and acetone or acetyl acetone on warming.

Hofmann,[3] by the interaction of acetaldehyde, mercuric oxide, and aqueous sodium hydroxide, only obtained aldehyde resin, but with paraldehyde a small quantity of a base was produced, $C_2Hg_6O_4H_2$, which corresponds to ethane hexamercarbide.

Later, the same investigator, using another mercuric salt, succeeded in obtaining a more definite compound.[4]

Chloratodimercuracetaldehyde,



forms colourless, lustrous prisms, more explosive than mercury fulminate. The compound is readily produced by the addition of an alcoholic solution of acetaldehyde to a solution of mercuric oxide in aqueous chloric acid. When treated with potassium hydroxide or cyanide, aldehyde resin is produced.

Auld and Hantzsch,[5] from acetaldehyde and mercuric oxide in slightly alkaline solution, obtained a base, trimercuridialdehyde hydroxide, which readily polymerised to a white powder, $(C_4H_8O_5Hg_3)_x$. The latter decomposes without melting at about 100° C. and is insoluble in the usual organic solvents, decomposed by dilute hydrochloric acid with formation of acetaldehyde and mercuric chloride, but not affected by dilute acetic acid. The investigators state that this is a delicate test for the presence of small quantities of acetaldehyde, since it detects the presence of one part of aldehyde in 6000 parts of water.[6]

[1] Lasserre, *J. Pharm. Chim.*, 1905, [vi.], **22**, 246; *Chem. Centr.*, 1905, ii. 1125.
[2] Leys, *J. Pharm. Chim.*, 1905, [vi.], **22**, 107; *Bull. Soc. chim.*, 1905, [3], 33, 1320.
[3] Hofmann, *Ber.*, 1898, 31, 1904.
[4] Hofmann, *ibid.*, 1905, 38, 1999.
[5] Auld and Hantzsch, *Ber.*, 1905, 38, 2684.
[6] For chloratotrimercuracetaldehyde, perchloratomercuracetaldehyde, and nitritodimercuracetaldehyde, see the action of acetylene on mercuric chlorate, perchlorate, and nitrate.

Derivatives of Ketones.

It was stated that aliphatic aldehydes or aldoses reduced mercuric acetate, but no such reduction is noticed with ketones or ketoses.[1] Nevertheless most investigators differ as to the products derived from ketones, and it is very difficult to say whether many of the compounds described are truly organometallic or merely complex addition products of the ketones. For the sake of readers interested in these derivatives, the following table is inserted to summarise these compounds of doubtful structure. The ketone used in these investigations was acetone.

PRODUCTS DERIVED FROM ACETONE AND MERCURIC SALTS.

Mercury Salt Used.	Product Isolated.	References.
Alkaline mercuric acetate.	$Me_2CO.2HgO$.	Lasserre, *J. Pharm. Chim.*, 1905, [vi.], **22**, 246.
Conc. mercuric sulphate solution.	$3Me_2CO.5HgO.5H_2SO_4$.	Bülmann, *Ber.*, 1902, **35**, 2584.
Mercuric sulphate.	$Me_2CO.3HgO.2HgSO_4$.	Denigès, *Ann. Chim. Phys.*, 1899, [7], **18**, 382; *Bull. Soc. chim.*, 1898, [3], **19**, 494, 751.
Mercuric oxide, sodium hydroxide.	$C_3Hg_3H_7O_3$.	Hofmann, *Ber.*, 1898, **31**, 1904; Kutscherow, *Ber.*, 1884, **17**, 20.
Mercuric chloride in alkaline solution.	$2Me_2CO.3HgO$.	Reynolds, *Chem. News*, 1871, **23**, 217; *Ber.*, 1871, **4**, 483.
Mercuric sulphate.	$4Me_2CO.9HgO.6HgSO_4$. $Me_2CO.3HgO.2HgSO_4$.	Oppenheimer, *Ber.*, 1899, **32**, 986; Hofmann, 1898, **31**, 399.
Mercuric chloride, ammonium chloride, hydroxylammonium chloride.	$2Me_2CO.5HgCl_2.2NH_4Cl.2(NH_2OH.HCl)$.	Grigorowitsch, *Chem. Zentr.*, 1906, i. 743.
Mercuric sulphate.	$5Me_2CO.12HgO.8HgSO_4$.	Denigès, *Ann. Chim. Phys.*, 1907, [8], **12**, 401.
Do.	Using monochloroacetone, $MeCOCH_2Cl.3HgO.2HgSO_4$.	Denigès, *Ann. Chim. Phys.*, 1899, [7], **18**, 382.

The work now to be described relates to compounds from acetone, which are far more definite in constitution, although very complex.

Interaction of Acetone and Mercuric Cyanide.[2]—To a solution of 11 grams of mercuric cyanide in 120 c.c. of ethyl or 30 c.c. of methyl alcohol is added 1·5 grams of sodium in 40 c.c. of alcohol. After twenty-four hours any precipitate is filtered off and 1·25 grams of acetone added to the clear solution; a dense white precipitate is formed, which is filtered off and washed free from cyanide. This product is decomposed by dilute hydrochloric acid, yielding acetone and hydrogen cyanide:

$$C_5H_2ON_2Hg_3 + 6HCl = C_3H_6O + 2HCN + 3HgCl_2$$

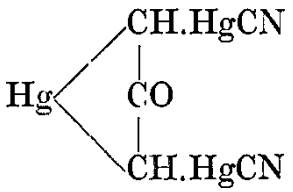
[1] Lasserre, *J. Pharm. Chim.*, 1905, [vi.], **22**, 246.

[2] Marsh and Fleming Struthers, *Trans. Chem. Soc.*, 1905, **87**, 1878; *Proc. Chem. Soc.*, 1905, **21**, 248.

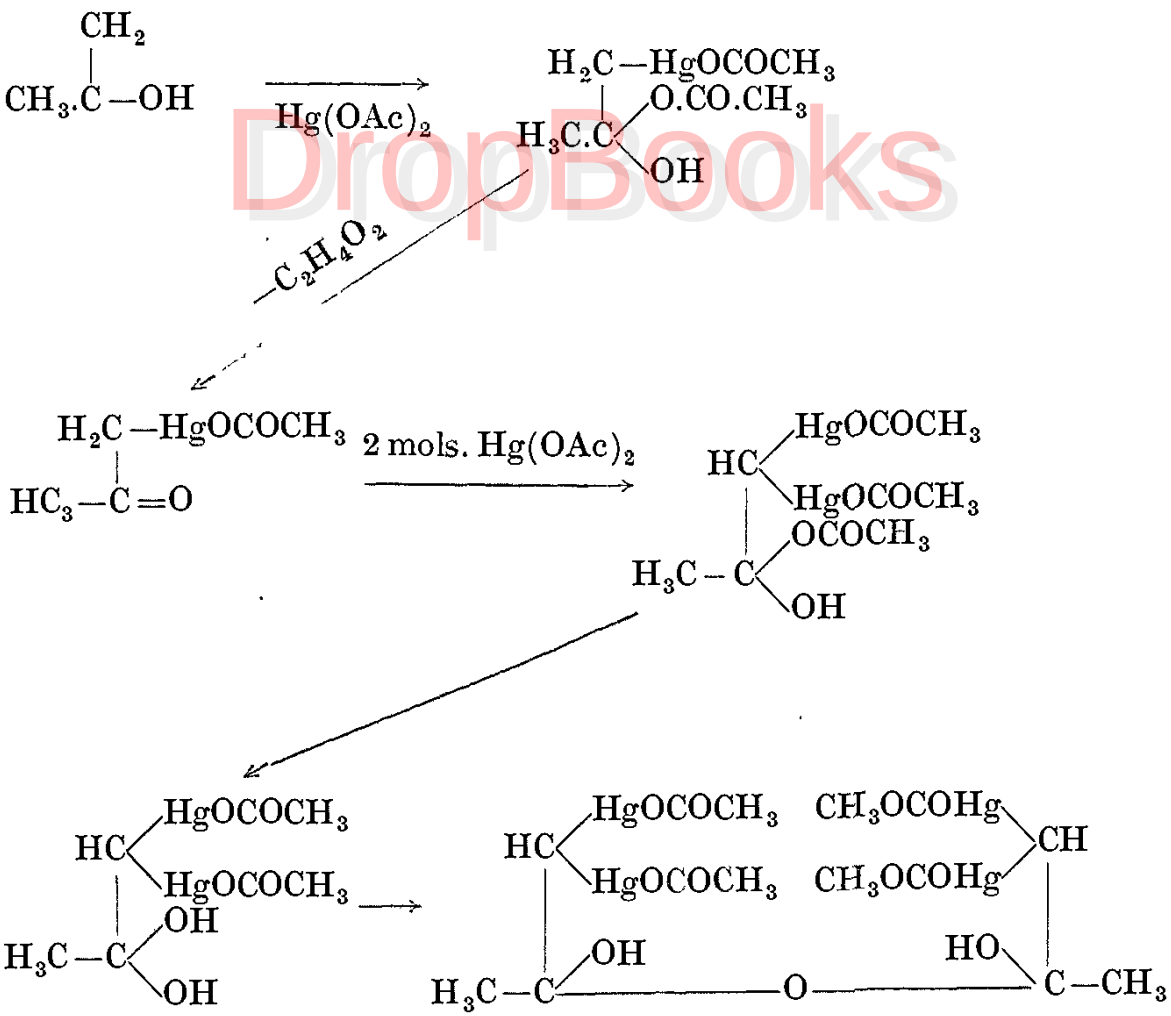
A similar product is formed when acetone and mercuric cyanide react in presence of sodium hydroxide, and the reaction may occur according to the equation :

$$C_3H_6O + 3Hg(CN)_2 = C_5H_2ON_2Hg_3 + 4HCN$$

The constitution assigned to the compound is

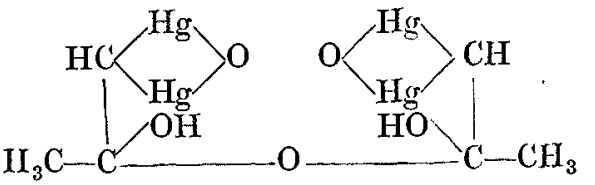


Tetra-acetoxymercuri diacetone hydrate.—This substance is prepared as follows :[1] 25 grams of dry powdered mercuric acetate and 50 grams of acetone (made from bisulphite compound) are heated under pressure at 100° C. for two hours. The solution after cooling and filtering does not produce a yellow coloration when treated with potassium hydroxide. Evaporation on the water-bath gives a yellow oil, which is taken up in 95 per cent. alcohol, and after a time white flocks appear. These are filtered off, washed with alcohol, and recrystallised from alcohol containing a few drops of acetic acid, the resulting product melting at 157° C. The course of the reaction is probably as follows, the acetone reacting in the enolic form :—



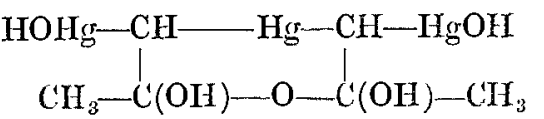
[1] Sand and Genssler, *Ber.*, 1903, 36, 3699.

This acetate, treated with 20 per cent. hydrochloric acid and potassium cyanide solution, splits up into acetone and mercury salt; whilst potassium hydroxide gives the corresponding *tetra-hydroxy-mercuri* compound. An aqueous solution of the acetate when decomposed with 10 per cent. potassium hydroxide yields a white precipitate of an *oxide* having the constitution :



This oxide is insoluble in water and organic solvents. The acetate with sodium chloride or oxalates yields the corresponding salts, the former being a very insoluble compound possessing no melting-point.

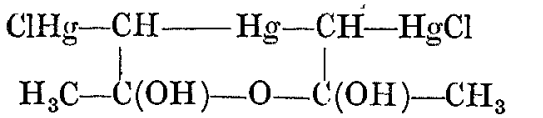
Tri-mercuri diacetone hydroxide,[1]



The mercuric oxide precipitated from 20 grams of mercuric chloride is well washed, and whilst moist treated with a solution of about 6 c.c. of acetone in 100 to 150 c.c. of water, a few drops of baryta added, and the whole well shaken until a solution is obtained. The baryta is precipitated by carbon dioxide, the latter removed by a current of air, and the barium carbonate filtered off. Evaporation of the filtrate on the water-bath gives a thick syrup, which forms a clear solution in water and reacts slightly alkaline. Its electrical conductivity is as follows :—

$$\left.\begin{array}{ll}\mu=0{\cdot}018, & v=256\\ \mu=0{\cdot}022, & v=512\end{array}\right\}\text{at } 18^\circ \text{ C.}$$

Dilute hydrochloric acid gives the corresponding *dichloride,*



as a colourless powder, easily soluble in aniline or pyridine, with difficulty in alcohol, and practically insoluble in water. When heated it becomes yellow and melts at about 110° C.

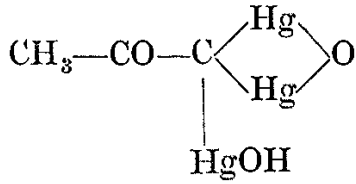
It forms a *platinichloride,* an amorphous product exploding suddenly at 178° C.

The corresponding *dibromide* forms small white needles, M.pt. 127° C., which are soluble in warm alcohol, ether, or pyridine. The *di-iodide* is so easily decomposed by acids that it cannot be prepared in the same way as the foregoing compounds. The base is first treated with potassium iodide, then with dilute acetic acid, when a faint yellow precipitate is obtained. This consists of small needles, M.pt. 104° C., which are insoluble in water, more soluble in alcohol or ether.

The base forms a *picrate* which contains 6 mols. of water of crystallisation, and is somewhat soluble in hot water; its conductivity, μ, is 0·042, at a dilution, v, of 1100 at 25° C.

[1] Auld and Hantzsch, *Ber.*, 1905, 38, 2684.

When the base is exposed to sunlight or treated with acids or alkali it is converted to an insoluble polymer.[1] The base or its polymer, when boiled with alkali, is decomposed, yielding water, acetone, and acetone mercarbide, which is identical with Hofmann's compound,



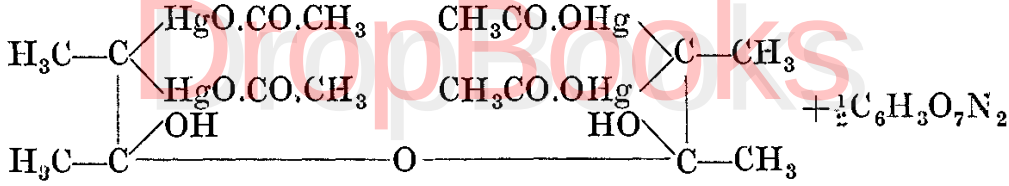
Concentrated hydrogen halides or oxyacids also decompose the base, immediately, giving acetone and a mercuric salt. Bromine in potassium bromide with the base yields mercuric bromide and *as*-dibromoacetone; whilst hydrogen sulphide precipitates mercuric sulphide from the base.

Derivative of Methylethyl Ketone.

From this ketone, by means of mercuric acetate, Lasserre[2] is stated to have obtained a compound of similar constitution to the one he isolated from acetone,

$$(COMeEt)_2.3HgO$$

By using the same methods as for acetone Sand and Genssler[3] isolated a body resembling that from the lower ketone. When this compound is treated with alcoholic picric acid it yields a picrate, which crystallises from benzene-acetic acid and has had the following oxonium constitution assigned to it :—



With the above exception, none of the higher ketones yield derivatives of definite constitution.

[1] See Reynolds, *Chem. News*, 1871, **23**, 217; *Ber.*, 1871, **4**, 483.
[2] Lasserre, *J. Pharm. Chim.*, 1905, [vi.], **22**, 246.
[3] Sand and Genssler, *Ber.*, 1903, **36**, 3699.

DropBooks

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CHAPTER V.

MERCURY (*continued*).

Derivatives of Aliphatic Acids—Derivatives of Formic Acid.

The following compounds, although written as derivatives of formic acid, have never been obtained from the acid or its esters. The formulæ assigned to them below are those due to Schoeller, Schrauth, and Essers,[1] although Manchot [2] considers them to be molecular addition compounds of the type CO.Hg(OR)X.

Acetoxymercuriformic methyl ester, $AcOHg.CO_2Me$.—The preparation and details for isolating this compound are the same as those given for the preparation of acetoxymercuri-ethylmethyl ether, the ethylene in the latter experiment now being replaced by carbon monoxide. The yield is 88 per cent. It crystallises in stellate aggregates of fine needles, M.pt. 110° C., easily soluble in alcohols or chloroform, sparingly in warm water, acetic acid, acetone, or benzene, and with difficulty in ether or petroleum ether. Carbon monoxide is split off when the salt is warmed or treated with 5-Normal hydrochloric acid, and the salt is decomposed by gentle warming with dilute sulphuric acid. Gently warmed with nitric acid it yields carbon dioxide: Aqueous or alcoholic ammonia splits out metallic mercury. When treated with dilute hydrochloric acid the *chloride* is obtained, long needles, M.pt. 110° C. The *bromide* crystallises in white plates, decomposing at 127° to 128° C., and the *iodide* has a similar appearance but is very easily decomposed.

Acetoxymercuriformic ethyl ester is prepared by the action of carbon monoxide on an ethyl alcohol solution of mercuric chloride, but the absorption takes three times as long as in methyl alcohol. The compound sinters at 65° C. and melts at 125° C. It is easily soluble in acetone, chloroform, or ethyl acetate, less so in warm water, ether, or benzene, sparingly in cold water, and insoluble in ligroin or petroleum ether. It crystallises in warty needles. The *chloride* crystallises in plates, melting at 88° C. with decomposition; the *bromide* and *iodide* are similar compounds. A *sulphide* has also been obtained as a yellowish-white precipitate.

Derivatives of Acetic Acid.

Bromomercuri-acetic acid, $HgBr.CH_2.CO_2H$.—A methyl alcoholic solution of ethanol mercuric bromide is treated with bromine and potassium hydroxide, a white crystalline precipitate being obtained.

[1] Schoeller, Schrauth, and Essers, *Ber.*, 1913, 46, 2869.
[2] Manchot, *Ber.*, 1920, 53, 984.

It crystallises in colourless needles, M.pt. 198° C., not decomposed by hydrochloric acid. With potassium iodide solution a yellow *iodide* is formed.

Some bromide is formed when ethanol mercuric bromide is oxidised by permanganate, but the main product of the reaction is oxalic acid.[1]

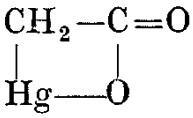
Anhydride of hydroxymercuri-acetic acid.[2]—This derivative is not obtained by direct mercuration of the acid or its derivatives, but by degradation of malonic acid derivatives.

(*a*) Mercury malonic ester (10 grams) is vigorously shaken with 100 c.c. (about 4·5 mols.) of normal sodium hydroxide at 37° C. for three hours, when a clear solution is obtained, which is allowed to remain at the same temperature for a further twelve hours. After filtering and diluting with 200 c.c. of water, 110 c.c. of Normal sulphuric acid are added, when white flocks separate, and carbon dioxide is evolved. The reaction is then brought to completion by allowing the mixture to remain on the water-bath for several hours, after which the precipitate is filtered off and washed free from sulphuric acid by decantation with hot water. The product is then dried *in vacuo* over phosphorus pentoxide, when a horny mass is obtained. Yield 5 to 5·6 grams, which is some 90 per cent. of the theory.

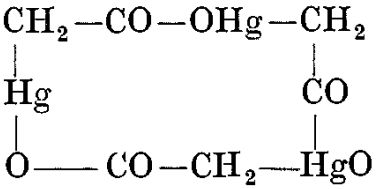
(*b*) Malonic acid (100 grams) and 120 grams of solid sodium hydroxide (about 3 mols.) are dissolved in 300 to 400 c.c. of water and heated to boiling, when 200 grams of precipitated mercuric oxide (1 mol.) are slowly added during half an hour. The oxide goes into solution, and the liquid is then diluted to about 1500 c.c. by the addition of 950 grams (1·5 mols.) of sulphuric acid (15·9 per cent.). It takes several hours to evolve the carbon dioxide completely, after which the product is filtered off and washed free from sulphuric acid, a nearly theoretical yield being obtained.

DropBooks

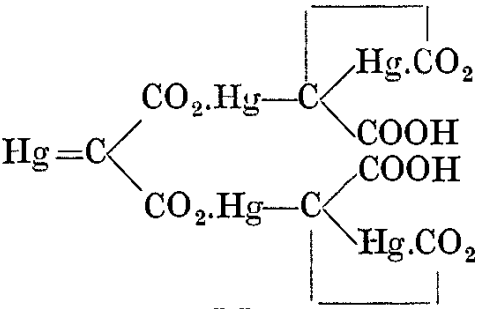
Mono- and trimolecular formulæ have been proposed for the compounds I. and II., whilst Biilmann believes that the preparation (*b*) yields a product to which he gives formula III.[3]



I.



II.



III.

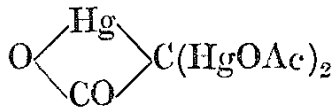
The anhydride towards 200° C. becomes brown, and at 250° C. explodes. It is insoluble in the usual solvents, but soluble in alkalies and alkali salts, yielding *hydroxymercuri-acetic acid*, $HOHg.CH_2.COOH$.

The *sodium salt* of this acid is obtained by dissolving the anhydride in 1 mol. of sodium hydroxide and evaporating the solution in the absence of carbon dioxide. Needles are deposited, which are fairly soluble in water, giving a solution alkaline to litmus, but the salt is insoluble in

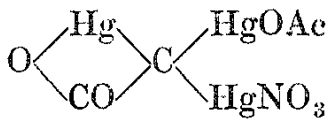
[1] Sand and Singer, *Annalen*, 1903, 329, 166.
[2] Schrauth and Schoeller, *Ber.*, 1908, 41, 2090; German Patents, 208634, 213371.
[3] Biilmann and Witt, *Ber.*, 1909, 42, 1067.

the usual organic solvents. When treated with ammonium sulphide, mercury sulphide is precipitated, and with solutions of metallic salts the difficultly soluble metallic salts of the acid are precipitated, *e.g.* *copper* sulphate yields $(HOHg.CH_2COO)_2Cu$. The *calcium*, *silver*, *mercury*, and *lead* salts are white powders.

Anhydride of hydroxymercuri-diacetoxymercuri-acetic acid.[1]—Dry mercuric acetate and freshly distilled acetic anhydride are heated at 100° C., until a test portion of the solution gives no precipitate of mercuric oxide, when treated with sodium hydroxide. A mercury derivative of acetic acid is thus obtained as a fine micro-crystalline precipitate, having the composition :

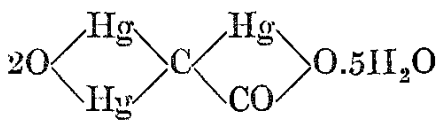


This acetate is insoluble in organic solvents, dissolves with decomposition in hydrochloric acid, but is soluble in cold 20 per cent. nitric acid with formation of a *nitro-acetate*,

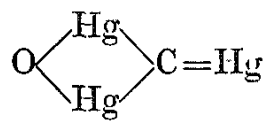


which may be precipitated by the addition of a large bulk of water.

Both the above compounds are non-explosive, but the free *base* prepared by decomposing the diacetate with cold potassium hydroxide is an exceedingly explosive compound. It is colourless, easily soluble in cold 20 per cent. hydrochloric acid or in potassium cyanide solution, and has the constitution :

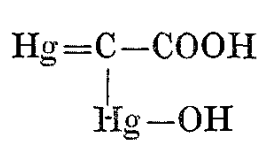


When heated to 160° C. it loses water and carbon dioxide, forming probably a methane derivative,



This compound when reduced by sodium amalgam yields mercuric acetate, whilst potassium iodide forms the corresponding *iodide*.

Mercuri-hydroxymercuri-acetic acid,[2]



The sodium salt of the acid is obtained when sodium acetate, mercuric oxide, and concentrated alkali are heated together at 110° to 120° C. for two to three hours and the melt extracted with water. The residue remaining is a polymer of the preceding compound, and is insoluble in

[1] Sand and Singer, *Ber.*, 1903, 36, 3707.
[2] Hofmann, *Ber.*, 1899, 32, 870 ; *Chem. Zentr.*, 1899, i. 1024.

alkali or acids. It dissolves, however, in nitric acid, and addition of water precipitates the *nitrate*,

$$[(NO_3Hg.)(Hg=)C.COOH]_x$$

as a yellowish-white crystalline mass, which decomposes on heating or on treatment with hot dilute hydrochloric acid or potassium cyanide. Sodium carbonate or 5 per cent. potassium hydroxide converts this nitrate to the *hydroxide*, but prolonged warming with concentrated alkali yields salts. A potassium hydroxide solution of the nitrate on addition of alcohol gives a precipitate of a yellow *potassium* salt of the formula,

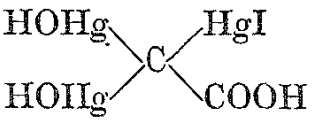
$$C_2Hg_2O_3HK.C_2Hg_2O_3H_2.2H_2O,$$

and this is decomposed by dilute hydrochloric acid to the *chloride*,

$$(ClHg)_2HC.COOH.$$

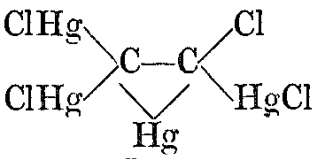
The *nitrate* of mercuri-hydroxymercuri-acetic acid is precipitated from alkaline solution by dilute nitric acid as a voluminous precipitate, which crystallises from 10 per cent. nitric acid in long needles.

Dihydroxymercuri-iodomercuri-acetic acid,

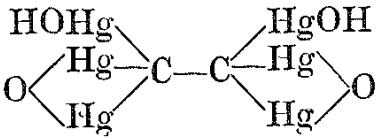


Whereas mercuri-hydroxymercuri-acetic acid derivatives are formed when sodium acetate, mercuric oxide, and concentrated alkali are heated together, the replacement of the oxide by mercuric iodide leads to the production of the sodium salt of the above iodomercuri compound when the action is carried out at 105° C. The derivative crystallises in yellow plates, which are only decomposed with difficulty by hydrochloric or hydrobromic acids. The *free acid* is obtained by the action of dilute nitric acid on the sodium salt, and it crystallises in greenish-white plates, which are partly decomposed by hot dilute hydrochloric acid, and completely by potassium cyanide solution, whilst potassium iodide gives a strongly alkaline liquid which is yellow. This *iodide* with dilute silver nitrate solution gives the *nitrate*, $(NO_3Hg)(HOHg)_2.C.COOH$, as a yellowish-white crystalline powder, which decomposes on heating, and is insoluble in water or 3 per cent. nitric acid, but soluble with partial decomposition in hydrochloric acid, potassium cyanide, or iodide solutions.

Trichloromercuri-acetic acid, $(ClHg)_3C.COOH$.—When an alcoholic solution of mercuric chloride is boiled for twenty hours with sodium ethylate, acetate, or propionate, the mercarbide, $C_2Hg_4Cl_4$, is obtained in glistening scales. It is soluble in hot alkali, and dilute hydrochloric acid precipitates the above chloride from the solution, a black residue remaining, which is a mixture of mercury with di- and trimercuri-acetic acid. The mercarbide, I., when warmed with sodium hydroxide or potassium cyanide, is decomposed, mercury separating and a strong odour of aldehyde resin being noticed. Heating with mercuric oxide and potassium hydroxide at 105° to 110° C. gives the explosive base II.:



I.

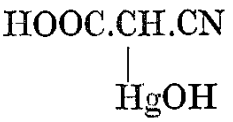


II.

Halogen substituted acetic acids have not been investigated to any great extent as to their capacity for forming mercury derivatives. Hofmann [1] isolated the compound, HgCl.CHCl.COOH.KCl, by boiling sodium monochloroacetate with mercuric oxide and alkali in aqueous solution. The compound crystallises from alcohol in silky needles, which are decomposed by dilute hydrochloric acid into mercuric chloride, potassium chloride, and glycol; by sodium hydroxide into mercuric oxide and sodium glycollate.

Derivatives of Cyanoacetic Acid.[2]

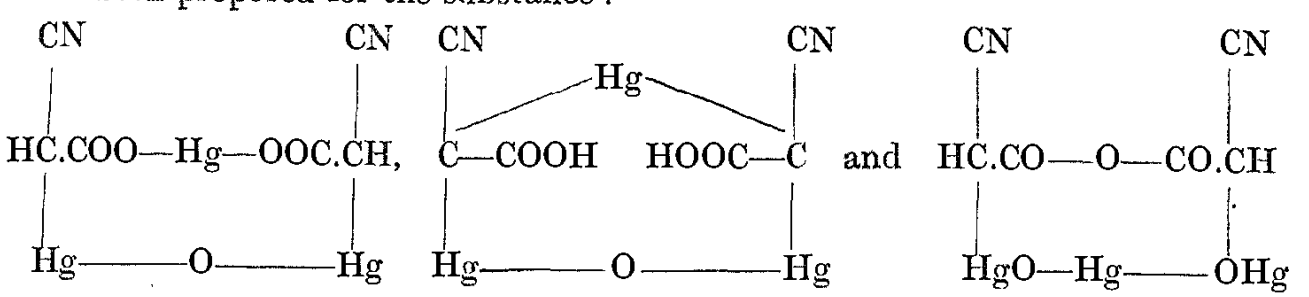
Hydroxymercuricyanoacetic acid,



When 3·24 grams of mercuric oxide (0·015 mol.) and 1·7 grams of cyanoacetic acid (0·02 mol.) in 30 c.c. of water are shaken together for two days, the mercuric oxide dissolves and a white crystalline precipitate is deposited (4·4 grams), which is soluble in alkalies forming salts. Attempts to prepare the same compound from aqueous cyanoacetic acid and mercuric acetate failed to give the same result. The *sodium* salt of the acid is obtained in good yield when sodium cyanoacetate is shaken with mercuric oxide, and the *potassium* and *barium* salts are prepared in the same way. The potassium salt is also obtained when mercuric cyanide and potassium cyanoacetate react in alkaline solution.

The *ethyl ester* is prepared by adding an aqueous solution of mercuric acetate (3·36 grams in 100 c.c.) to the ethyl ester of cyanoacetic acid in methyl alcohol (2·4 grams in 60 c.c.), when 6·2 grams of the ester separate as a snow-white crystalline precipitate. The *methyl ester* is also crystalline and prepared in a similar manner.

By treating a neutral solution of mercuric nitrate with ammonium cyanoacetate, Meves [3] obtained a mercury compound of indefinite composition. Petterson, by adding ammonium cyanoacetate solution, 0·02 mol., to an aqueous solution of mercuric acetate, 0·03 mol., obtained in two days a white flocculent precipitate, which split off mercuric oxide when treated with sodium carbonate. The following formulæ have been proposed for the substance :—



[1] Hofmann, *Ber.*, 1899, 32, 870; *Chem. Zentr.*, 1899, i. 1024.
[2] Petterson, *J. prakt. Chem.*, 1912, 86, 462.
[3] Meves, *Annalen*, 1867, 143, 204.

Derivatives of Benzoylacetic Acid.[1]

Anhydro-α-hydroxy-mercuribenzoyl acetic acid, $C_6H_3.CO—CH—CO—O—Hg$.—Three grams of benzoyl acetic acid in 50 c.c. of chloroform are boiled for one minute with an excess of yellow mercuric oxide and filtered. The filtrate is evaporated to dryness, the residue extracted twice with ether and dried. Yield 1·3 grams. The compound is white, decomposes at about 290° C., and is readily soluble in hot chloroform or sodium hydroxide, but insoluble in water or ether. Dilute hydrochloric acid decomposes it, forming mercuric chloride and benzoyl acetic acid.

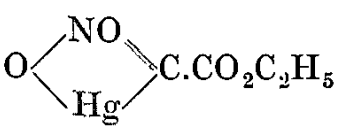
Mercury-bis-benzoylmethane, $(C_6H_5COCH_2)_2Hg$.—Five grams of yellow mercuric oxide are added to 1·3 grams of benzoyl acetic acid in 50 c.c. of 95 per cent. alcohol, the mixture heated to boiling and filtered. The residue is boiled with 20 c.c. of alcohol, filtered, and the two filtrates combined. Dilution with water and cooling in ice yields 0·8 gram of a very pale yellow precipitate, M.pt. 159·5° C. The compound is soluble in hot alcohol or acetone, but insoluble in water or ether. An alcoholic solution of the compound does not give a precipitate of mercuric oxide when treated with sodium hydroxide, but ammonium sulphide gives an immediate precipitate of mercuric sulphide. With mercuric chloride it yields the following compound :—

Benzoylmethyl-mercuric chloride.—The above compound in hot 95 per cent. alcohol is heated with mercuric chloride until the mixture no longer gives a test for mercuric ions when treated with sodium hydroxide. The mixture, after dilution and cooling in ice, gives a precipitate melting at 146° C. This compound is identical with that prepared by the direct mercuration of acetophenone, *i.e.* phenacyl-mercuric chloride, see p. 196.

DropBooks

Derivatives of Nitro-acetic Esters.[2]

Ethyl hydroxymercuri-aci-nitro-acetate anhydride,



This compound is formed as a white precipitate from the interaction of ammonium *aci*-nitro-acetate and mercuric chloride in aqueous solution. It sublimes when carefully heated, detonates when strongly heated, and when ignited burns with a luminous flame. In bases it dissolves readily, but is almost insoluble in boiling water. Treatment with bromine in potassium bromide solution forms ethyl dibromonitro-acetate, and potassium iodide removes the mercury from the anhydride as mercuric iodide.

Prager considered the formation of the anhydride to be preceded by the formation of *ethyl chloromercuri-aci-nitro-acetate,*

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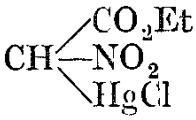
[1] Kharasch and Staveley, *J. Amer. Chem. Soc.*, 1923, 45, 2966.

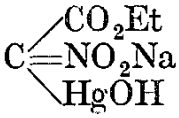
[2] Scholl and Nyberg, *Ber.*, 1906, 39, 1956; Prager, *Monatsh.*, 1912, 33, 1285; Steinkopf, *Annalen*, 1923, 434, 21.



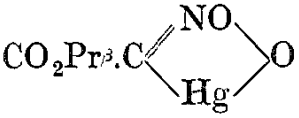
and it is probable that this compound is formed when the anhydride dissolves in dilute hydrochloric acid, and the corresponding *cyanide* when potassium cyanide is used as solvent.

The *sodium aci-nitro* compound is a greenish-yellow substance, formed when the anhydride is dissolved in sodium hydroxide and the solution evaporated with exclusion of atmospheric carbon dioxide.

The following formula has been assigned to it :—



iso-Propyl hydroxymercuri-aci-nitro-acetate anhydride,



is formed when mercuric chloride is added to an aqueous solution of the ammonium salt of isopropyl *aci*-nitro-acetate in the presence of sodium acetate, and the *isobutyl* and *isoamyl* derivatives may be prepared in the same way. The general physical properties of these compounds are the same as those of the above ethyl derivative, save that potassium iodide does not react with their alkaline solutions.

Derivatives of substituted Acetic Acids.[1]

Many investigators have attempted to isolate mercury derivatives from aceto-acetic ester, but the results have been so varied that no reliance can be placed on any of the early work on this compound. Kharasch and Staveley,[2] however, have obtained definite results by heating mercury salts of substituted acetic acids *in vacuo*, *e.g.* dimethyl and diethyl aceto-acetic acids when dried and heated *in vacuo* at 90° C. evolve carbon dioxide, and the mercury becomes bound to the carbon atoms which were formerly attached to the carboxyl groups :—

$$[CH_3CO.CEt_2.CO_2]_2Hg \xrightarrow{\text{Heat}} [CH_3CO.CEt_2-]_2Hg + 2CO_2$$

Mercury bis-α-acetyl-α-isopropyl or **Mercury-bis-aceto-dimethyl-methane**, $[CH_3CO.CMe_2-]_2Hg$.—Mercuric dimethyl aceto-acetate is heated in a vacuum at 90° C., when it is found to lose two molecular equivalents of carbon dioxide, which is shown by the loss in weight. The resulting mass is extracted with acetone, and the solvent removed *in vacuo*, the product isolated melting at 120° C. It is soluble in acetone, alcohol, toluene, or xylene, but only slightly soluble in ether. Mercuric sulphide is split off from it by the action of ammonium sulphide, but no mercuric oxide is formed when sodium hydroxide is added. The compound soon decomposes with the deposition of metallic mercury.

[1] Hellon and Oppenheim, *Ber.*, 1877, 10, 701 ; Hofmann, *Ber.*, 1898, 31, 2212 ; Ley, *Ber.*, 1900, 33, 1014 ; Biilmann, *Ber.*, 1902, 35, 2585 ; Michael, *Ber.*, 1905, 38, 2090.

[2] Kharasch and Staveley, *J. Amer. Chem. Soc.*, 1923, 45, 2961.

Aceto-dimethyl-methyl-mercuric chloride, $CH_3CO.CMe_2$—HgCl.—To 1·8 grams of the preceding compound in 15 c.c. of alcohol, 1·4 grams of mercuric chloride dissolved in 30 c.c. of 95 per cent. alcohol are added, and the whole boiled for five minutes. On cooling, white crystals, M.pt. 124·5° C., are deposited. Yield 1·1 grams.

In a similar manner, commencing with mercuric *aa*-diethylaceto-acetate, the following compounds have been obtained, their properties being analogous to those of the methyl compounds :—

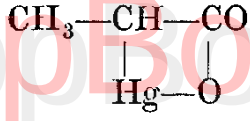
Mercury bis-*α*-acetyl-*α*-ethylpropyl or **Mercury bis-aceto-diethylmethane,** $[CH_3CO.CEt_2—]_2Hg$, M.pt. 109° C.; **Aceto-diethyl-methyl-mercuric chloride,** $[CH_3CO.CEt_2—]HgCl$, M.pt. 77° C.

Diazo-acetic Esters.[1]—Mercuric oxide dissolves in the cooled ethyl ester of diazo-acetic acid, and the product is extracted with ether. From the ethereal solution yellow, rhombic crystals of *mercury bis-diazo-acetic ethyl ester* are deposited, the parameters of which are a : b : c = 0·4546 : 1 : 0·72527. The crystals melt with decomposition at 104° C., and are affected by direct sunlight, mercury separating out. The substance explodes on concussion and is volatile in steam, with some decomposition.

The methyl ester yields a similar compound which melts with partial decomposition at 123° C., and is less soluble in ether than the ethyl derivative. The methyl compound is decomposed by water at ordinary temperatures into mercury, nitrogen, methyl alcohol, oxalic and glycollic acids.

Derivatives of Propionic Acid.

Anhydride of *α*-hydroxymercuripropionic acid,[2]



Hydroxymercuri methyl malonic ester, $HOHg.CMe(CO_2Me)_2$, is saponified with 4 mols. of Normal alkali hydroxide and the resulting solution acidified by dilute sulphuric acid. The precipitate is washed, suspended in water and boiled until the evolution of carbon dioxide ceases, a nearly quantitative yield of ester being obtained. It decomposes at 150° C., and with halogen acids yields mercuric salts. It is insoluble in organic solvents, but dissolves readily in alkalies.

***β*-Mercury bis-propionic acid,** $Hg(CH_2.CH_2.CO_2H)_2$.[3]—This derivative is isolated by reducing *β*-iodopropionic ethyl ester in cold ethereal solution with 0·5 per cent. sodium amalgam. The residue is shaken with warm Normal sodium hydroxide solution, then cooled and acidified with dilute sulphuric acid, which precipitates colourless crystals. Yield 27 per cent. It is recrystallised from hot water, and melts at 148·5° to 149·5° C. (corr.). It is easily soluble in warm alcohol, less so in acetone or hot ethyl acetate, and sparingly in ether or chloroform. It is soluble in hot concentrated hydrobromic acid, the solution depositing crystals of an acid on cooling. Heated with water at 100° C. the acid forms the *anhydride* of *β-hydroxymercuripropionic acid*. This decomposes at 190° C., and is insoluble in the usual organic solvents or water, but soluble in alkalies or warm mineral acids.

[1] Curtius and Buchner, *J. prakt. Chem.*, 1888, [2], 38, 411 ; Buchner, *Ber.*, 1895, 28, 215.
[2] Schoeller and Schranth, *Ber.*, 1909, 42, 782.
[3] Fischer, *Ber.*, 1907, 40, 387.

Derivatives of Malonic Acid and its Esters.[1]

Mercury bis-malonic methyl ester, $Hg[CH(COOMe)_2]_2$.—Methyl malonate (36 grams, $2\frac{1}{3}$ mols.), with 25 grams of mercuric oxide (1 mol.) and 50 c.c. of water, are shaken on a machine at 37° C., in the absence of light. After twelve hours a white body having the above composition separates out. It is soluble in cold chloroform and sparingly in alcohol, acetone, or ethyl acetate. It sinters at 125° C. and melts at 127° C. (corr.). Saponification with 4 mols. of Normal alkali, and acidification with dilute sulphuric acid, gives an almost quantitative yield of the anhydride of hydroxymercuri-acetic acid.

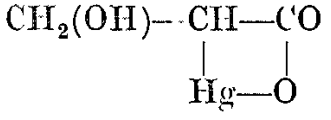
Hydroxymercuri methyl malonic methyl ester, $HOHg.CMe(CO_2Me)_2$.—The preparation is carried out in a similar manner to the above, using equal molecules of the ester and mercuric oxide and continuing the shaking for several days. It is a white amorphous solid, insoluble in the usual solvents. When saponified as above it gives an 85 per cent. yield of the anhydride of hydroxymercuri-propionic acid. In a similar manner the *methyl ester* of *ethylmalonic acid* yields 80 per cent. of hydroxymercuributyric acid anhydride.

From malonic acid itself, Biilmann claims to have obtained several very complex derivatives, but their constitution seems doubtful.[2]

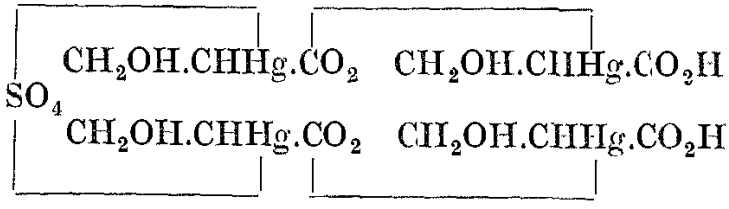
Derivatives of Unsaturated Acids.[3]

The acids of this series can be mercurated, with the exception of fumaric and mesaconic acids, which only yield normal mercuric salts.

Anhydride of α-hydroxymercuri-β-hydroxypropionic acid,



Five grams of anhydrous acrylic acid are mixed with a solution prepared from 10 grams of mercuric oxide in 10 c.c. of sulphuric acid and 40 c.c. of water. Addition of alcohol gives a white, sticky precipitate, the latter on treatment with alcohol becoming gritty. It is filtered off, washed, and dried, and is very hygroscopic. The yield from two preparations was 8 to 9 grams. Biilmann assigns the following constitution to this body:—



If the substance be boiled with 8 to 10 parts of water, a part of it dissolves; the insoluble residue, washed with water and alcohol and dried, gives the pure anhydride.

[1] Biilmann, *Ber.*, 1902, 35, 2580; Schoeller and Schrauth, *ibid.*, 1908, 41. 2089; German Patents, 208634, 213371.

[2] See German Patents, 221483, 231092, 248291.

[3] Biilmann, *Ber.*, 1902, 35, 2571.

It has also been prepared by heating mercurous acrylate, the following reaction taking place :—

$$Hg_2(CH_2{=}CH.CO_2)_2+H_2O=Hg+CH_2{=}CH.CO_2H+CH_2OH.\overline{CHHg.CO_2}$$

Anhydride of α-hydroxymercuri-β-hydroxy-n-butyric acid,[1]

$$CH_3—CHOH—CH—CO$$
$$\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad Hg—O$$

Seven grams of crystallised crotonic acid in 50 c.c. of warm water are heated with 7 grams of mercuric oxide until complete solution takes place. The solution is then evaporated to about 25 c.c., cooled, and treated with 200 c.c. of absolute alcohol. The white precipitate is washed with alcohol and ether, and dried over calcium chloride.

The anhydride may also be prepared by the interaction of crotonic acid and mercuric acetate, precipitating the product with alcohol.

Mercuration of crotonic acid using mercuric sulphate solution does not yield a pure compound.

Derivative of α-acetoxymercuri-β-hydroxysuccinic acid,

$$\begin{matrix} HO—CH—CO_2 \\ \qquad\quad | \qquad\quad \diagdown \\ AcO.Hg—CH—CO_2 \end{matrix} \diagup Hg.\ 2H_2O$$

Mercuric acetate, 20 grams, is dissolved in 60 c.c. of water and treated in the cold with 5 grams of maleic acid in 40 c.c. of water. Any precipitate which may be formed is filtered off. 4 grams of maleic acid in 40 c.c. of water added, and the mixture heated, a white micro-crystalline precipitate separating out. This is filtered off and washed with very dilute acetic acid, then with water, alcohol, and ether. Yield 7·5 grams. It is insoluble in water and alcohol, but dissolves in acids or alkalies. It reacts with sodium chloride and potassium iodide solutions according to the equations :

$$C_6H_6Hg_2O_7+3NaCl=\begin{matrix} HOCH—CO_2Na \\ \quad | \\ ClHg.CH—CO_2Na \end{matrix}+C_2H_3O_2Na+HgCl_2$$

$$C_6H_6Hg_2O_7+4KI=C_2H_3O_2K+C_2H_2(CO_2K)_2+2HgI_2+KOH$$

Derivative of anhydro α-hydroxymercuri-α-hydroxymethyl succinic acid,

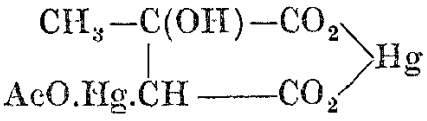
$$(HO.CH_2.\overline{C(CO_2Hg).CH_2.CO_2})_2Hg \text{ or } (\overline{Hg.CH_2.C(CO_2)(OH).CH_2.CO_2})_2Hg$$

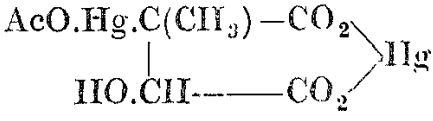
When prepared by the mercuration of itaconic acid using mercuric sulphate solution, 7 grams of acid and 50 c.c. of the salt solution yield 11 grams of product. It contains 3 molecules of water of crystallisation and has similar properties to the preceding compound.

Derivative of Citraconic Acid.—Five grams of the acid in 40 c.c. of water are added to a cold solution of 20 grams of mercuric acetate in 60 c.c. of water. When heated at 60° C. this mixture yields a micro-

[1] Ley, *Ber.*, 1900, 33, 1010; Billmann, *loc. cit.*

crystalline precipitate, which is filtered whilst hot. It is washed with very dilute acetic acid, water, and alcohol. Yield 8 grams. The following constitution has been assigned to it :—



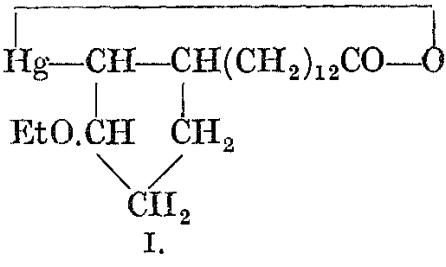
or


It is insoluble in water or alcohol, but dissolves in acids. Ammonium sulphide precipitates mercuric sulphide from its alkaline solutions.

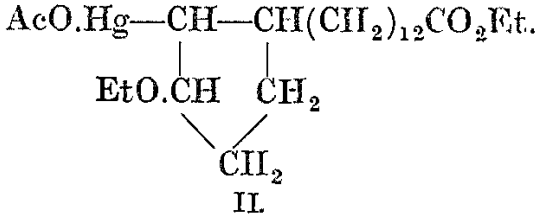
Derivatives of Chaulmoogric Acid.[1]

Anhydride of hydroxymercuri-ethoxy-chaulmoogric acid.—To 1 mol. of mercuric acetate dissolved in 2000 c.c. of hot absolute alcohol and 400 c.c. of glacial acetic acid, and cooled to room temperature, 1 mol. of chaulmoogric acid is added in small portions, with constant stirring, until a fairly clear solution is obtained. After twenty-four hours any sediment is filtered off and the filtrate allowed to stand in an ice-chest for three months. A total of 50 grams of crystals is thus obtained, and recrystallised from 95 per cent. alcohol. A mass of silvery, minute needles is formed, melting at 112° to 113° C., to a clear liquid. It is readily soluble in chloroform or glacial acetic acid, less so in hot alcohol, hot ethyl acetate, or hot acetone, and practically insoluble in cold solvents. Its constitution is represented by formula I.

Ethyl acetoxymercuri-ethoxy-chaulmoograte (II.).—One mol. of freshly distilled ethyl chaulmoograte and 1·25 mols. of mercuric acetate are dissolved in 1000 c.c. of absolute alcohol and 100 c.c. of glacial acetic acid. The solution is tightly stoppered and allowed to stand for ten days in an ice-chest, then filtered, and the filtrate poured into a large volume of water. An oil is obtained, and if the water be separated off, the oil partially solidifies on standing. It is filtered and the residue recrystallised from petroleum ether, then from absolute alcohol. Yield 15 grams. It forms minute, colourless needles, M.pt. 67° to 68° C., stable in air, but decomposed by inorganic acids.[2]



I.



II.

[1] German Patent, 245571; Dean, Wrenshall, and Fujimoto, *J. Amer. Chem. Soc.*, 1925, 47, 403.

[2] The patent mentioned above (German Patent, 245571) also deals with the mercuration of cyclohexenecarboxylic ester.

The following German patents have also been taken out for aliphatic acid mercurials: *Ibid.*, 246207, behenolic acid esters, stearolic acid ester. *Ibid.*, 264267, alyl hydroxy fatty acids. *Ibid.*, 279199, aminomethane disulphonic acid. *Ibid.*, 228877, oleic acid ethyl ester, triolein. *Ibid.*, 387850; American Patent, 1457675; diethyl diallylmalonate, diallylbarbituric acid, ethyl diallylacetate, diethyl o-phenylenediacrylate, diphenic acid and ethyl diphenylamine-2-carboxylate.

The following deal with *purine* derivatives: Rosenthaler and Abelmann, *Ber. Deut. pharm. Ges.*, 1923, 33, 186; German Patents, 282376, 282377.

*

CHAPTER VI.

MERCURY (*continued*).

Aromatic Compounds of the Types R_2Hg; $RHgR'$; $RHgX$.

All the compounds of the type R_2Hg, with the exception of mercury dibenzyl, the bromo-, chloro-, and nitrophenyls, and thienyl derivatives, have been prepared by the amalgam method. The amalgams used are more concentrated than for the corresponding alkyls, and a higher temperature is required for the reaction; the strength of amalgam in certain cases is as follows: Mercury diphenyl, 2·7 per cent.; mercury di-o-tolyl, 8 per cent.; mercury di-m-tolyl, 3 per cent.; mercury di-m-xylyl, 2 per cent.; mercury dipseudocumyl, 1·5 per cent.; mercury di-α-naphthyl, 4 per cent. The Grignard reagent has not been used so extensively in these preparations as with the alkyls, but it is the sole method of obtaining mercury dibenzyl, and has also been applied to the production of mercury diphenyl and dicyclohexyl. A recent method of preparation consists in treating phenylmercuric or halogenated phenylmercuric halides with copper in pyridine solution, and in this way mercury diphenyl, di-p-chlorophenyl, di-p-bromophenyl, and di-o-nitrophenyl have been isolated. Stannous chloride and sodium hydroxide in pyridine have also been used instead of copper in the case of the phenyl compound. It has already been noted that ethyl hydrazine reacts with mercuric oxide to yield mercury diethyl, and phenyl hydrazine in the same way yields mercury diphenyl. The halogens attack mercury diphenyl, giving $PhHgHal.$, but in the case of bromine or iodine the reaction proceeds a stage further if four atoms of halogen are used, as shown by the equations:

$$R_2Hg + 2Hal. = RHgHal. + RHal.$$
$$RHgHal. + 2Hal. = RHal. + HgHal._2$$

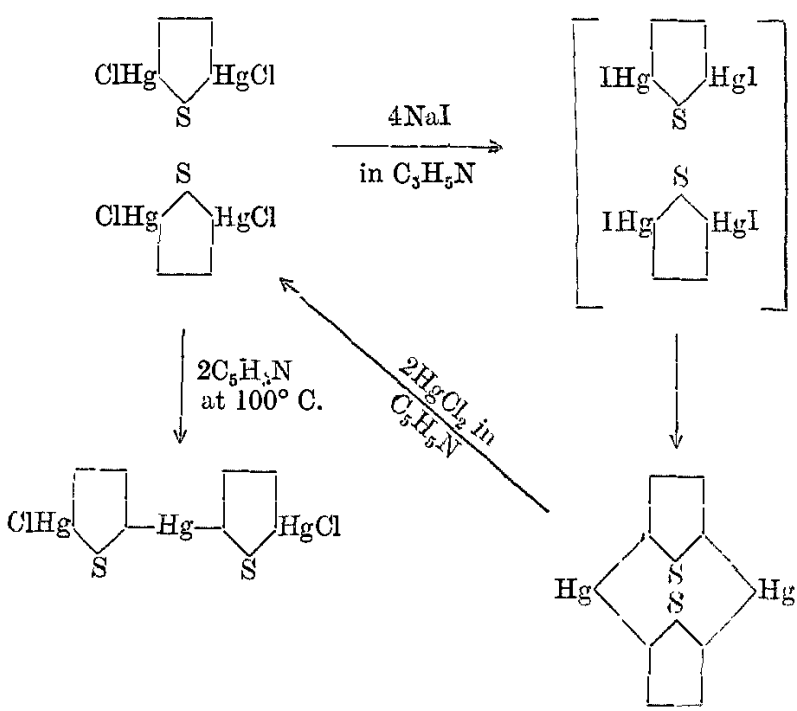
A similar series of reactions also occurs when mercury di-α-naphthyl is treated with iodine in carbon disulphide solution.

Gaseous hydrogen chloride, bromide, or iodide decompose mercury diphenyl, whereas hydriodic acid forms phenylmercuric iodide. Concentrated hydrochloric acid varies in its action towards these derivatives. Whilst mercury diphenyl, di-o-nitrophenyl, di-p-tolyl, di-α-naphthyl, di-β-naphthyl are decomposed when boiled with concentrated hydrochloric acid, mercury di-m-xylyl, dipseudocumyl, and bis-diphenyl remain unchanged. Concentrated nitric acid decomposes mercury diphenyl, di-p-tolyl, and di-α-naphthyl, di-β-naphthyl, and sulphuric acid gives similar results. When boiled with organic acids, mercury diphenyl forms salts of the type RHgX, and mercury di-α-naphthyl behaves in a similar manner towards glacial acetic acid, but when heated

DropBooks

in a sealed tube with the latter acid mercury dibenzyl is decomposed. As far as investigations have gone, the following chlorides react with the type R_2Hg to yield organometallic compounds: boron, indium, thallium, phosphorus, and arsenic trichlorides and silicon tetrachloride, likewise the metals magnesium, zinc, cadmium, aluminium, selenium, and tellurium. Mercury diphenyl reacts with mercuric chloride in acetone or alcoholic solution to give phenylmercuric chloride, but if mercurous chloride is used a temperature of 160° C. is necessary to effect the change. Mercuric halides or cyanides react with mercury dicyclohexyl in any solvent to yield the type RHgX, and the halides give a similar result with mercury di-α-naphthyl. Bromine also splits off a naphthyl group from the latter compound.

The foregoing reactions do not necessarily apply to R_2Hg when R = thienyl, and these compounds come under a category of their own. All the compounds of this type are prepared from halidemercuri thiophenes, the method of conversion depending on the position of the substituents in the thiophene ring. It was found that attempts to produce the iodide from 2-chloromercuri thiophene by the action of sodium iodide in acetone solution gave only small yields, but a considerable amount of mercury 2 : 2′-dithienyl was formed at the same time. Investigation showed that this method of producing the type R_2Hg is a general one, if the mercury residue be in the α-position, and in the case of 5-chloromercuri-2-benzylthiophene the change is brought about by sodium thiocyanate in acetone solution. Di-substituted thiophenes containing methyl groups in the 3 : 4 or 3 : 5 positions react in a similar manner, but if these groups are in the 2 : 5 positions the conversion cannot be brought about by sodium iodide. 3-Chloromercuri-2 : 5-dimethylthiophene is transformed to 2 : 5 : 2′ : 5′-tetramethyl-3 : 3′-dithienyl by boiling it in xylene solution with metallic sodium, and the corresponding 2 : 5-diphenylthiophene undergoes a like change. The reactions of 2 : 5-dichloromercurithiophene are interesting and are illustrated in the scheme below. It will be seen that the change from RHgX to R_2Hg may be also brought about by heat in this case.



The dithienylenes, one of which is shown above, are non-crystalline insoluble powders, only decomposing at high temperatures.

The type RHgR′ is much less stable than R_2Hg, and in all cases these unsymmetrical compounds have been obtained by aid of the Grignard reagent. In order to obtain satisfactory yields, the Grignard reagent should not be used in large excess, and the temperature should be kept below 5° C. Mercury ethyl phenyl decomposes after standing for several months into mercury diethyl and mercury diphenyl, and a similar change takes place with mercury ethyl benzyl. At ordinary temperatures mercury phenyl benzyl is slowly transformed into mercury diphenyl and mercury dibenzyl, but at 80° C. the decomposition produces mercury, dibenzyl, and mercury dibenzyl. Mercury o-tolyl benzyl at 80° C. yields mercury, dibenzyl, and mercury di-o-tolyl. All compounds of this type when treated with alcoholic mercuric chloride split according to the equation :

$$RHgR' + HgCl_2 = RHgCl + R'HgCl$$

With alcoholic hydrogen chloride, one compound of the type RHgCl is always formed, and sometimes both radicles give chlorides, but no general rule can be formulated from the known compounds to cover all cases.

Some methods of preparing derivatives of the type RHgX have already been dealt with in describing the reactions of the type R_2Hg. In the case of benzene and toluene the mercuration may be carried out directly, using mercuric acetate. If the operation is performed in the presence of alcohol, benzene may be converted to phenylmercuric acetate at 100° C., but the process takes about fifty-five hours to obtain an 80 per cent. yield. When toluene is refluxed with mercuric acetate, ortho- and para- ring-substituted compounds are produced. Another method is to treat the aryl sulphinic acids or their sodium salts with mercuric chloride, when the following reaction occurs :—

$$R.SO_2H + HgCl_2 = RHgCl + SO_2 + HCl$$

This reaction has been applied to phenyl and tolyl derivatives. The acid grouping of aryl boric acids may also be replaced by mercury, this affording one means of preparing phenyl, tolyl, and benzyl compounds.

$$RB(OH)_2 + HgCl_2 + H_2O = RHgCl + HCl + H_3BO_3$$

The Grignard reagent has been employed in isolating the mercuric halides of the following radicles : phenyl, tolyl, benzyl, and naphthyl,

$$RMgX + HgX_2 = RHgX + MgX_2$$

If the compound RHgX be treated with a second molecule of Grignard reagent, the type R_2Hg is produced.

Triphenylstibine when heated with mercuric chloride yields phenylmercuric chloride, and tri-m-tolylstibine mercurichloride when boiled with alcohol is converted into m-tolylmercuric chloride.

Although thienyl compounds of the type RHgX react with potassium iodide in acetone to give the type R_2Hg, this has only been noted in benzenoid derivatives in the case of p-tolylmercuric chloride, when a large excess of potassium iodide is used. With phenyl and α-naphthylmercuric chlorides only the corresponding iodides are produced. The

iodides in the tolyl series are obtained by refluxing the other halides with alcoholic potassium iodide, and pseudocumylmercuric iodide is only formed by heating the R_2Hg derivative with an excess of alcoholic mercuric iodide in a sealed tube at 130° to 140° C.

The nitrates of the phenyl, tolyl, and α-naphthyl compounds are formed by the action of oxides of nitrogen on the R_2Hg derivatives as well as by alcoholic silver nitrate on the halides.

In the case of halogen-substituted hydrocarbons the principal method used is the mercuration of the sulphinic acid, and not the hydrocarbon itself, whilst the method acts equally well with nitrobenzene. The nitrotoluenes when mercurated by mercuric oxide in the presence of sodium hydroxide yield compounds containing mercury in the side chain, but with mercuric acetate at 140° C., in the absence of a solvent, the mercury enters the ring. If nitrotoluene sulphinic acids are used as starting-points, the acid group is replaced by mercury by prolonged boiling with 50 per cent. aqueous alcoholic mercuric chloride.

The sulphonic acids are mercurated directly by means of mercuric acetate in boiling aqueous solution in the presence of acetic acid.

Thiophene is readily mercurated by mercuric chloride in the presence of sodium acetate, yielding mono- and di-mercurated products of the type RHgX, but not R_2Hg. Mono-substituted thiophenes usually behave in a similar manner, and in the case of di-substituted thiophenes the position of the groups in the nucleus determines whether a di-mercurated product is formed, although all yield monomercuri compounds. The bromides are obtainable from the chlorides by using mercuric bromide in alcoholic solution, or from the corresponding dithienyls by treatment with mercuric bromide in acetone solution. Replacement of the mercuric bromide by sodium iodide (1 mol.) in acetone solution gives the iodides, the bromides RHgX being used instead of the chlorides.

Compounds of the Type R_2Hg.

Mercury diphenyl, Ph_2Hg, may be prepared in several ways, as follows :—

1. From phenylmercuric acetate.[1] It was first noted by Dimroth that phenylmercuric acetate when treated with alkaline sodium stannite gives mercury diphenyl, and this reaction has recently been worked up by Maynard and shown to be the best method of preparation yet discovered, the yield being approximately 96 per cent. A solution containing 50 grams of stannous chloride in 125 c.c. of water and 125 c.c. of cold 40 per cent. sodium hydroxide is added with mechanical stirring to 30 grams of phenylmercuric acetate in 300 c.c. of water. After stirring for one hour, mercury and mercury diphenyl separate, the mass being filtered, washed, and dried. The mercury diphenyl is extracted from the residue by 150 c.c. of acetone, and the compound precipitated by the addition of water. Yield 13·2 grams. The reaction may be represented by the equation

$$2C_6H_5HgX + Na_2SnO_2 + 2NaOH = (C_6H_5)_2Hg + Hg + 2NaX + Na_2SnO_3$$

2. Two other phenyl mercuric compounds have also been mentioned

[1] Dimroth, *Ber.*, 1902, 35, 2853; Maynard, *J. Amer. Chem. Soc.*, 1924, 46, 1510.

as yielding mercury diphenyl, (1) phenylmercuric bromide, by prolonged boiling with potassium sulphide,

$$2PhHgBr + K_2S = 2KBr + HgS + Ph_2Hg$$

and (2) phenylmercuric iodide, when treated with sodium amalgam in alcohol or benzene solution.

$$2PhHgI + H_2 = 2HI + Hg + Ph_2Hg$$ [1]

3. By the Grignard reaction.[2] Twenty-five grams of bromobenzene and 3·1 grams of magnesium in dry ether are slowly treated with 13 grams of mercuric chloride and the mixture boiled for one hour on the water-bath. The mass is then decomposed with dilute hydrochloric acid and the whole extracted with ether, the ethereal solution yielding about 7·5 grams of mercury diphenyl. Yield 44 per cent. Magnesium phenyl bromide with phenyl mercuric chloride gives a 67 per cent. yield of mercury diphenyl.

4. By the Fittig reaction.[3] In this case bromobenzene, mercuric chloride, and metallic sodium are allowed to react in dry benzene. After completion of the reaction the mercury diphenyl is obtained from the benzene solution.

5. By the use of sodium amalgam.[4] Equal volumes of bromobenzene and xylene containing one-tenth by volume of ethyl acetate are treated with an excess of 2·7 per cent. sodium amalgam and heated from 120° to 140° C. for eight hours. The mercury diphenyl is obtained from the benzene-xylene solution in 46 per cent. yield.

6. From phenylmercuric sulphide, phenylmercuric thiocarbonate, and phenylmercuric thiosulphate.[5]

The above three compounds are changed to mercury diphenyl by treatment with alcohol, benzene, and sodium thiosulphate respectively.

7. From phenylarsenious oxide.[6] Thirty-four grams of phenylarsenious oxide in 300 c.c. of 2-Normal sodium hydroxide are stirred with 54·2 grams of mercuric chloride in 500 c.c. of water, the temperature being maintained at 0° C. The temperature is then raised by heating on a water-bath until no further precipitate is formed, and afterwards the product is filtered, washed, and dried. The mercury diphenyl is removed from this residue by boiling with alcohol, from which the compound crystallises on cooling.

8. From phenylhydrazine.[7] Phenylhydrazine is heated with an excess of yellow mercuric oxide, when nitrogen is evolved, and aniline and mercury diphenyl formed. Ten grams of the base yield 4 grams of pure compound. A similar result is obtained when mercury acetamide replaces the oxide.

9. By the action of copper on a pyridine solution of phenylmercuric bromide.[8]

[1] Dreher and Otto, *Annalen*, 1870, 154, 93.
[2] Pfeiffer and Truskier, *Ber.*, 1904, 37, 1125.
[3] Michaelis and Reese, *Ber.*, 1882, 15, 2877.
[4] Dreher and Otto, *loc. cit.*; *Ber.*, 1869, 2, 542; Ladenburg, *Annalen*, 1874, 173, 151; Michaelis, *Annalen*, 1876, 181, 290; Aronheim, *Annalen*, 1878, 194. 148.
[5] Pesci, *Gazzetta*, 1899, 29, (1.), 394.
[6] German Patent, 272289.
[7] Forster, *Trans. Chem. Soc.*, 1898, 73, 783; Fischer and Ehrhard, *Annalen*, 1879, 199, 332.
[8] Hein, Wagler, and Retter, *Ber.*, 1925, 58, [B], 1505.

10. From the compound produced by the action of ammonia on phenyl mercuric acetate.[1]

The compound $(C_6H_5Hg)_2NH_2OAc$ reacts with carbon bisulphide in alcoholic solution according to the equation :

$$(C_6H_5Hg)_2NH_2.C_2H_3O_2+CS_2=(C_6H_5)_2Hg+HgS+C_2H_4O_2+CNSH$$

Similar results are obtained if the carbon bisulphide is replaced by diphenyl- or p-ditolylthiocarbamides.

11. The production of mercury diphenyl was noticed when bromobenzene, chloroformic ester, and sodium amalgam interact in the production of esters of benzoic acid.[2]

12.[3] A solution of 6·2 grams of phenylmercuric chloride in 40 c.c. of pyridine is treated with 2·5 grams of stannous chloride in 5 c.c. of water and sufficient 30 per cent. sodium hydroxide to give solution. The mixture is filtered after several hours. Yield 3·1 grams, 90 per cent.

Mercury diphenyl crystallises in small, felted needles, M.pt. 124·5° C., B.pt. 204° C. at 10·5 mm. The melting-point as given by various investigators ranges between 120° to 126° C., and the variation is no doubt due to the presence of small quantities of diphenyl, which is always formed at the same time. The crystals turn yellow when exposed to light, are soluble in chloroform, benzene, ether, or alcohol, and insoluble in water. Its density varies between 2·29 and 2·34. No absorption bands are shown by chloroform solutions of mercury diphenyl at any dilution.[4]

The reactions of mercury diphenyl are summarised in the following table :—

REACTIONS OF MERCURY DIPHENYL.

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Chlorine.	Dry gas.	Phenylmercuric chloride, chlorobenzene, mercurous chloride.	Dreher and Otto, *Annalen*, 1870, 154, 93.
Bromine or Iodine.	Two atoms of halogen in alcohol or CS_2.	Phenylmercuric bromide or iodide, bromo- or iodobenzene.	do.
Bromine or iodine.	Four atoms of halogen.	Phenyl haloid, mercuric salt.	do.
Free thiocyanogen, $(SCN)_2$.	Ether solution.	Phenylmercuric thiocyanate.	Söderbäck, *Annalen*, 1919, 419, 266.
Hydrogen chloride, bromide, or Iodide.	..	Benzene, mercuric salt.	Dreher and Otto, *loc. cit.*

[1] Pesci, *Gazzetta*, 1909, 39, (i.), 147.
[2] Wurtz, *Compt. rend.*, 1869, 68, 1298.
[3] Steinkopf, Bielenberg, and Jensen, *Annalen*, 1923, 430, 71.
[4] Purvis and M'Cleland, *Trans. Chem. Soc.*, 1912, 101, 1514.

Reactions of Mercury Diphenyl—*continued.*

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Conc. hydriodic acid.	..	Phenylmercuric iodide.	Dreher and Otto, *loc. cit.*
Fuming nitric acid.	..	Carbon, benzene, nitrobenzene, mercuric nitrate.	Dreher and Otto. *Ber.*, 1869, **2**, 542; Otto, *J. prakt. Chem.*, 1870, [2], **1**, 179.
Glacial acetic acid.	Boil.	Phenylmercuric acetate, benzene.	Otto, *loc. cit.*; Dreher and Otto, *Annalen*, 1870, **154**, 93.
Formic, propionic, or myristic acids.	Boil.	Phenylmercuric salts, benzene.	Dreher and Otto, *loc. cit.*
Hypochlorous acid.	..	Same results as chlorine.	do.
Mercuric chloride.	Acetone or alcohol solution.	Phenylmercuric chloride.	Steinkopf. *Annalen*, 1917, 413. 310; Otto, *loc. cit.*
Mercurous chloride.	In alcohol at 160° C.	Phenylmercuric chloride, metallic mercury.	Otto, *loc. cit.*
Mercuric cyanide or thiocyanate.	Alcoholic solution at 120°.	Phenylmercuric salts.	do.
Mercuric acetate.	(1) Alcoholic solution at 120° C. for 1 hour.	Phenylmercuric acetate.	do.
	(2) Without a solvent at 150° C., and excess of acetate.	1·4·Diacetoxymercuribenzene, 1·2·4·triacetoxy· and 1·2·4·5·tetra-acetoxymercuribenzenes.	Posci, *Atti. R. Accad. Lincei*, (5), 8, i, 130; *Chem. Zentr.*, 1899, i. 734.
Mercuric oxide.	Sealed tube at 180° C.	Phenylmercuric oxide.	Otto, *loc. cit.*
Oxides of nitrogen :—	..	..	Bamberger, *Ber.*, 1897, 30, 506.
N_2O_3.	..	Phenylmercuric nitrate, benzene diazoniim nitrate.	
N_2O_4.	..	Phenylmercuric nitrate, nitrosobenzene.	
N-Bromoacetamide.	Dry benzene solution.	Phenylmercuric bromide, methyl isocyanate.	Kharasch, *J. Amer. Chem. Soc.*, 1921, 43, 1888.
N-Bromobenzamide.	do.	Phenylmercuric bromide.	
m-Nitro-N-bromobenzamide.	do.	m-Nitrocarbanilide.	
Do. o- and p-nitro compounds.	do.		
Sulphur.	Alcoholic solution at 140° C.	Diphenylsulphide, mercuric sulphide.	Dreher and Otto, *Ber.*, 1869, **2**, 542.

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Reactions of Mercury Diphenyl—*continued.*

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Thionyl chloride.	Heat.	Phenylmercuric chloride.	Hermann and Köchlin. *Ber* 1883, 16, 1625.
Benzene sulphonic chloride.	Benzene solution at 160° C.	Phenylmercuric chloride, diphenyl sulphone.	Otto, *Ber.*, 1885, 19, 246.
Toluene sulphonic chloride (*p*).	Benzene solution at 120° C.	*p*-Tolylmercuric chloride, phenyl-tolyl sulphone.	
Sulphur trioxide.	..	Mercury benzene sulphonate.	Otto, *J. prakt. Chem.*, 1870, 1 [2], 179.
Allyl iodide.	..	Phenylmercuric iodide, diallyl, diphenyl.	Saida, *Monatsh.*, 1880, 1, 715.
Ethylene dibromide.	..	Dibenzyl, mercuric bromide.	Dreher and Otto, *loc. cit.*
Benzal chloride.	At 150° C.	Phenylmercuric chloride, triphenylmethane.	Kekulé and Franchimont. *Ber.* 1872, 5, 906.
Phenyl iodo dichloride.	Aqueous solution.	Phenylmercuric chloride, diphenyl iodonium chloride.	Willgerodt, *Ber.*, 1898, 31, 915.
Lithium, sodium, potassium.			
Copper.	..	Mercury, diphenyl.	Dreher and Otto, *loc. cit.*
Magnesium.	..	Magnesium diphenyl.	Hilpert and Grüttner. *Ber.*, 1913 46, 1675; Fleck, *Annalen* 1893, 276, 138.
Zinc.	Boil for two minutes in hydrogen atmosphere.	Zinc diphenyl.	Hilpert and Grüttner, *loc. cit.* Dreher and Otto, *loc. cit.*
Cadmium.	In hydrogen atmosphere.	Cadmium diphenyl.	Hilpert and Grüttner, *loc. cit.*
Boron trichloride.	At 180°–200° C. for several hours.	Phenyl boron chloride, mercuric chloride.	Michaelis, *Ber*, 1889, 22, 241.
Phenyl boron chloride.	At 300°–320° C. for 24 hours.	Diphenyl boron chloride.	Michaelis, *Ber.*, 1894, 27, 244.
Aluminium.	At 140° C. for 10–15 seconds in hydrogen or nitrogen atmosphere.	Aluminium triphenyl, mercury, aluminium amalgam.	Hilpert and Grüttner, *Ber.*, 1912 45, 2828.
Indium trichloride.	..	Indium diphenyl chloride.	Goddard and Goddard, unpublished.
Thallic chloride.	Ether or benzene solution.	Thallium diphenyl chloride, phenylmercuric chloride.	Goddard, *Trans. Chem. Soc.* 1922, 121, 40.

Reactions of Mercury Diphenyl—*continued.*

Reacting Substance.	Conditions of Reaction.	Resulting Products.	References.
Zirconium tetrachloride.	Aqueous solution.	$ZrOCl_2$, 2PhHgCl, benzene.	Peters, *Ber.*, 1908, **41**, 3173: see *Annalen*, 1894, **282**, 320.
Silicon tetrachloride.	At 300° C.	Phenylmercuric chloride, phenyl silicon trichloride.	Ladenburg, *Annalen*, 1874, **173**, 152.
Stannic chloride.	..	Phenylmercuric chloride, tin diphenyl dichloride.	Aronheim, *Annalen*, 1878, **194**, 148.
Phosphorus trichloride.	Heat at 180° C.	Phenylmercuric chloride, phosphenyl chloride.	Schwarze, *J. prakt. Chem.*, 1874, **10**, (2), 222; Michaelis and Graeff, *Ber.*, 1875, 8, 922: Michaelis, *Annalen*, 1876, **181**, 290.
Arsenic trichloride (2 mols.).	Heat at 250° C.	Phenyl dichloro-arsine, mercuric chloride.	La Coste and Michaelis, *Annalen*, 1880, **201**, 196.
Arsenic trichloride (1 mol.).	Heat at 210° C. for several hours.	Diphenyl chloro-arsine, mercuric chloride.	
Phenyl dichloro-arsine (1 mol.).	..	Diphenyl chloro-arsine.	Michaelis and Link, *Annalen*, 1881, **207**, 193.
Phenyl dichloro-arsine (2 mols.).	..	Diphenyl chloro-arsine, mercuric chloride.	do.
Antimony trichloride.	Xylene solution at 130° C.	Triphenylstibine dichloride, Diphenylstibine trichloride.	Hasenbäumer, *Ber.*, 1898, **31**, 2911.
Bismuth.	Heat for 10 minutes at 250° C. in hydrogen atmosphere.	Triphenylbismuthine.	Hilpert and Grüttner, *Ber.*, 1913, **46**, 1675.
Bismuth tribromide.	Dry ether solution.	Triphenylbismuthine.	Challenger and Allpress. *Trans. Chem. Soc.*, 1921, **119**, 913.
Selenium.	..	Selenium diphenyl, selenium amalgam.	Krafft and Lyons, *Ber.*, 1894, **27**, 1768.
Tellurium.	..	Tellurium diphenyl, tellurium amalgam.	do.
Tellurium dichloride.	..	Chlorobenzene, tellurium amalgam.	do.
Acetyl chloride.	With or without benzene.	Phenylmercuric chloride, acetophenone.	Calvery, *J. Amer. Chem. Soc.*, 1926, **48**, 1009.
Benzoyl chloride.	do.	Phenylmercuric chloride, benzophenone.	do.
Ethyl chloroformate.	do.	Phenylmercuric chloride, benzophenone.	do.

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Mercury 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenyl, M.pt. 272° C., is formed when mercuric 2 : 4 : 6-trinitrobenzoate is heated to 180° C. When heated with alcoholic mercuric chloride it is converted into *2 : 4 : 6-trinitrophenylmercuric chloride*.[1]

Phenylmercury 2 : 4 : 6-trinitrophenyl, M.pt. 227·5° C., is obtained by heating phenylmercuric trinitrobenzoate in a vacuum at 222° C. It is decomposed by hydrogen chloride, yielding benzene and 2 : 4 : 6-trinitrophenylmercuric chloride.[2]

Mercury di-p-chlorophenyl.[3]—Five grams of p-chlorophenylmercuric chloride, 6·5 grams of copper and 35 c.c. of pyridine are allowed to stand for a day, then the mixture is saturated with carbon dioxide. An 81 per cent. yield, or 2·5 grams, of the mercury compound is obtained. It crystallises from hot acetone in white needles, M.pt. 242° to 243° C., readily soluble in pyridine, less soluble in warm chloroform or ether.

Mercury di-p-bromophenyl forms white needles, M.pt. 244° to 245° C., obtained in 92 per cent. yield. It is very soluble in pyridine, sparingly in cold acetone or ether.

Mercury di-o-nitrophenyl occurs in pale yellow needles, M.pt. 206° to 207° C., easily soluble in pyridine, hot acetone, and carbon disulphide, sparingly in carbon tetrachloride. Yield 92 per cent. When boiled with concentrated hydrochloric acid nitrobenzene is split off.

Tolyl Compounds.

Mercury di-o-tolyl may be prepared by the sodium amalgam method (see mercury diphenyl, Method 5). In this case 8 per cent. amalgam is used, and the yield is about 33 per cent.[4] The compound forms quadratic crystals from benzene, M.pt. 108° C.; B.pt. 219° C. at 14 mm. The reactions of mercury di-o-tolyl with the trichlorides of boron, phosphorus, and arsenic, also with nitrogen tri- and tetr-oxides, are similar to those described under mercury diphenyl (p. 74).

Mercury di-m-tolyl is prepared from m-bromotoluene using 30 per cent. sodium amalgam. From ethyl acetate it forms colourless needles, M.pt. 102° C., soluble in benzene, chloroform, or acetone, less soluble in alcohol or ether. Heated with phosphorus trichloride for twelve hours at 200° C. it yields m-tolyldichlorophosphine.

Mercury di-p-tolyl is best prepared according to the description of Whitmore as follows:[5] Forty grams of pure p-tolylmercuric chloride, 70 grams of sodium iodide (75 per cent. excess), 300 c.c. of 95 per cent. alcohol, are boiled for fifteen hours, the whole being vigorously stirred. After cooling and filtering the precipitate is washed with water until the washings no longer react with hydrogen sulphide. The product may be further purified if necessary by recrystallisation from xylene. Yield

[1] Kharasch, *J. Amer. Chem. Soc.*, 1921, 43, 2238.
[2] Kharasch and Grafflin, *J. Amer. Chem. Soc.*, 1925, 47, 1948.
[3] Heln, Wagler, and Retter, *Ber.*, 1925, 58, 1499.
[4] Michaelis, *Ber.*, 1895, 28, 589; *Annalen*, 1896, 293, 303.
[5] Whitmore, Hamilton, and Thurman, *J. Amer. Chem. Soc.*, 1923, 45, 1066; Peters, *Ber.*, 1905, 38, 2567.

of pure product, 80 per cent. The reaction takes places according to the equation :

$$2RHgCl + 4NaI = R_2Hg + 2NaCl + Na_2HgI_4$$

The compound may also be prepared from p-bromotoluene and sodium amalgam.[1]

The pure compound crystallises in needles. M.pt. 238° C., which are soluble in benzene, xylene, or chloroform, less soluble in alcohol, and insoluble in water. Mercury di-p-tolyl gives the same type of products as mercury diphenyl (see table, p. 74) when it reacts with halogens, halogen acids, mercuric chloride, boron or arsenic trichlorides, phosphorus trichloride,[2] silicon tetrachloride, nitrogen tri- and tetr-oxides,[3] sulphur, selenium, and tellurium.[4]

Treatment with concentrated nitric acid does not yield the hydrocarbon as with mercury diphenyl, but nitrotoluenes, and alkaline permanganate yields the tolylmercuric hydroxide, the presence of the latter being shown by changing it to the chloride. p-Toluene sulphonic iodide boiled with mercury di-p-tolyl in carbon tetrachloride solution yields tolylmercuric iodide, mercuric iodide, and tolyl sulphone, whilst the corresponding sulphonic chloride does not react under the same conditions.[5] (See p. 76.)

p-Tolylmercury 2 : 4 : 6-trinitrophenyl, M.pt. 203° C., is prepared in a similar manner to the phenyl compound from p-tolylmercuric trinitrobenzoate.[6]

Benzyl Compounds.

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The production of mercury dibenzyl appears to have been a matter of considerable difficulty.[7] Attempts to prepare it by the amalgam method failed, and the first successful preparation was made by use of Grignard's reaction.

Pope and Gibson[8] prepared **mercury dibenzyl** by the interaction of benzyl magnesium chloride and mercuric chloride in dry ether. This method was improved by Wolff,[9] and Jones and Werner,[10] the latter investigators obtaining a greatly increased yield by substituting benzylmercuric chloride for mercuric chloride; 3·8 grams of magnesium, 20 grams of benzyl chloride, and 35 grams of benzyl mercuric chloride, giving 40 grams of mercury dibenzyl. Another method has recently been described in which benzyl chloride is treated with an excess of magnesium dust, the liquid decanted off and mercuric chloride added to the solution. This mixture is boiled and shaken, then treated with dilute acetic acid and extracted with ether, from which the product crystallises.[11]

[1] Ladenburg, *Annalen*, 1874, 173, 162 ; Zeiser, *Ber.*, 1895, 28, 1670.
[2] Michaelis, *Annalen*, 1896, 293, 292.
[3] Kunz, *Ber.*, 1898, 31, 1528.
[4] Zeiser, *Ber.*, 1895, 28, 1670.
[5] Whitmore and Thurman, *J. Amer. Chem. Soc.*, 1923, 45, 1068.
[6] Kharasch and Grafflin, *J. Amer. Chem. Soc.*, 1925, 47, 1948.
[7] Canipisi, *Compt. rend.*, 1865, 61, 861 ; Wurtz, *Compt. rend.*, 1869, 68, 1300 ; Dreher and Otto, *Annalen*, 1870, 154, 176.
[8] Pope and Gibson, *Trans. Chem. Soc.*, 1912, 101, 735.
[9] Wolff, *Ber.*, 1913, 46, 64.
[10] Jones and Werner, *J. Amer. Chem. Soc.*, 1918, 40, 1257.
[11] Banús, *Anal. Fis. Quim.*, 1922, 20, 667.

Mercury dibenzyl may also be obtained in 75 per cent. yield by the action of copper on a pyridine solution of benzylmercuric chloride in the absence of air.[1]

Mercury dibenzyl crystallises in thin, lustrous, doubly refracting plates, readily soluble in chloroform or carbon tetrachloride, less soluble in benzene, ethyl acetate, or alcohol, and insoluble in ether or light petroleum. It is not decomposed when boiled with water, and gives no absorption bands.[2] When heated with glacial acetic acid in a sealed tube for seven hours at 160° to 170° C. it yields mercury, toluene, benzyl acetate, and dibenzyl.[3]

Mercury 2 : 4 : 2′ : 4′-tetranitrodibenzyl, $(C_6H_3(NO_2)_2.CH_2)_2Hg$, is obtained by heating mercuric 2·4-dinitrophenylacetate to 180° C. It melts at 235° C., and when heated in the dry state yields tetranitrodibenzyl.[4]

Xylyl Compounds.

Mercury di-o-xylyl crystallises in long needles, M.pt. 150° C., easily soluble in benzene, chloroform, or carbon disulphide, less soluble in ether or alcohol. It has never been prepared by any direct means, but was isolated as a by-product by the interaction of monobromo-o-xylol, $CH_3 : CH_3 : Br = 1 : 2 : 4$, sodium amalgam, and chloroformic ester.[5]

Mercury di-m-xylyl *is prepared by the addition of 150 grams of* 1·3·4-bromoxylene to 2 per cent. sodium amalgam and the mixture then heated for twelve hours at 140° to 150° C. The compound crystallises in fine needles, M.pt. 169° to 170° C., difficultly soluble in alcohol or cold ether, readily soluble in hot benzene. It is decomposed by hot hydrochloric acid into the hydrocarbon and mercuric chloride. Heated with phosphorous trichloride at 230° C. it yields m-xylylmercuric chloride and m-xylyldichlorophosphine, whilst arsenic trichloride gives m-xylyldichloro-arsine.[6]

Mercury di-p-xylyl is formed under similar conditions to the ortho-compound. It crystallises in prisms, M.pt. 123° C., and undergoes the same reactions as the meta derivative.

Higher Benzene Homologues.

Mercury dimesityl forms glistening silver needles, M.pt. 236° C., fairly soluble in benzene, less soluble in alcohol. Yield small.[7]

Mercury dipseudocumyl occurs as white prisms, M.pt. 189° C., and is less soluble in alcohol than the mesityl compound and not decomposed on prolonged heating with concentrated hydrochloric acid. It may be prepared in the usual way, using 1·5 per cent. amalgam.[8]

Mercury dipentamethylphenyl, $(C_6Me_5)_2Hg$, has been isolated from the interaction of sodium amalgam, bromopentamethyl benzene, and chloroformic ester, as small prisms, M.pt. 266° C. It distils at higher

[1] Hein, Wagler, and Retter, *Ber.*, 1925, 58, [B], 1507.
[2] Purvis and M'Cleland, *Trans. Chem. Soc.*, 1912, 101, 1514.
[3] Jones and Werner, *J. Amer. Chem. Soc.*, 1918, 40, 1257.
[4] Kharasch, *J. Amer. Chem. Soc.*, 1921, 43, 2238.
[5] Jacobson, *Ber.*, 1884, 17, 2372.
[6] Weller, *Ber.*, 1887, 20, 1718; Michaelis, *Annalen*, 1902, 320, 330.
[7] Michaelis, *Ber.*, 1895, 28, 588.
[8] Michaelis, *ibid.*

temperatures with partial decomposition and is easily soluble in hot xylene, less soluble in ether, and insoluble in alcohol.[1]

Mercury dicumyl yields white needles. M.pt. 134° C., soluble in alcohol, ether, chloroform, benzene, or xylene. It has a characteristic smell and is easily decomposed when heated with hydrochloric acid.[2]

Cyclohexyl Compounds.[3]

Mercury dicyclohexyl.—This compound proved more difficult to isolate than the phenyl derivative, but has been obtained by the action of mercuric bromide on a large excess of magnesium cyclohexyl bromide. It is much less stable than mercury diphenyl, decomposing even in a few hours to a black oil when kept over phosphorus pentoxide in the dark in a vacuum desiccator. Mercury dicyclohexyl forms white, hard granules, M.pt. 78° to 79° C., which are more soluble than mercury diphenyl, and combines directly with mercuric halides or cyanide in any solvent to form cyclohexylmercuric salts. It has also been prepared by the sodium amalgam method, when it is said to form white needles, M.pt. 139° C., which can be sublimed in small quantities *in vacuo*.[4]

Mercury di-4-methylcyclohexyl is a colourless liquid, density 1·459 at 21° C., and cannot be distilled without decomposition.

Diphenyl Derivatives.[5]

Mercury bis-diphenyl, $(C_6H_5.C_6H_4)_2Hg$.—Treatment of m-bromodiphenyl with sodium amalgam in the usual way gives a yield of 10 per cent. of the above product. It crystallises from benzene in small scales, which melt at about 216° C. and are almost insoluble in the usual solvents. Concentrated hydrochloric acid on prolonged boiling does not decompose the compound, and its *halogen derivatives* are only formed when it is heated in sealed tubes with mercuric halides. They are white crystalline powders, melting above 325° C.

Dimercury bis-diphenyl.—$Hg(C_6H_4—C_6H_4)_2Hg$ is the formula given to a body obtained when the above bromodiphenyl is replaced by dibromodiphenyl. Its composition appears to be doubtful.

Naphthyl Derivatives.

Mercury di-α-naphthyl, $(C_{10}H_7)_2Hg$.[6]—Bromonaphthalene is mixed with several times its volume of hydrocarbons, B.pt. 120° to 140° C., one-tenth of its volume of ethyl acetate, and the whole treated with a slight excess of 4 per cent. sodium amalgam. After boiling for eighteen hours the mixture is filtered hot, mercury dinaphthyl appearing in white, glistening, microscopic, rhombic columns on cooling. It has been more recently prepared by treating α-naphthylmercuric bromide in pyridine solution with copper.[7] The crystals, which melt at 243° C., are easily soluble in hot carbon bisulphide or chloroform, and may be reprecipi-

[1] Jacobson, *Ber.*, 1889, **22**, 1215.
[2] Michaelis, *Ber.*, 1895, 28, 588; Schiff, *ibid.*, 1877, 10, 1745.
[3] Grüttner, *Ber.*, 1914, 47, 1651.
[4] Tiffeneau and Gannagé, *Bull. Sci. Pharmacol.*, 1921, 28, 7.
[5] Michaelis, *Ber.*, 1895, 28, 592.
[6] Otto and Mordes, *Annalen*, 1868, 147, 164; Otto, *Annalen*, 1870, 154, 188.
[7] Hein, Wagler, and Retter, *Ber.*, 1925, 58, [B], 1507.

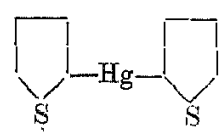
tated by alcohol or ether, also slightly soluble in benzene, insoluble in water.

When heated with concentrated halogen acids, naphthalene, mercury, and halogen halides are formed, but 15 per cent. aqueous hydrocyanic acid has no effect, even on prolonged heating. Dilute nitric acid decomposes mercury di-α-naphthyl, forming naphthalene, and fuming nitric acid gives nitronaphthalenes. Concentrated sulphuric acid yields mercuric sulphate and naphthalene sulphonic acid, whilst glacial acetic acid gives α-naphthylmercuric acetate and naphthalene. A solution of mercury di-α-naphthyl in acetone when boiled with mercuric chloride is converted to α-naphthylmercuric chloride.[1] Mercuric iodide when heated for one hour with mercury di-α-naphthyl in a sealed tube at 150° C. in alcoholic solution gives α-naphthylmercuric iodide. Mercuric bromide acts in a similar manner to the chloride when the reaction is carried out in alcohol in a sealed tube at 120° to 130° C., and bromine also gives naphthyl mercuric bromide under the same conditions. Iodine in carbon bisulphide yields the corresponding iodide, provided the halogen is not in excess, in the latter case the products are mercuric iodide and α-iodonaphthalene. Arsenic trichloride reacts to form α-naphthyldichloroarsine at high temperatures.[2] Nitrogen trioxide yields α-naphthyl mercuric nitrate and α-naphthyl diazonium nitrate, but nitrogen tetroxide yields no nitrate or diazonium compound. The following substances gave no product with mercury di-α-naphthyl: zinc, copper, or tin, the reaction being carried out in carbon disulphide; ethyl iodide: alcoholic hydrogen sulphide; sodium amalgam, the reaction being conducted in alcoholic solution.

Mercury di-β-naphthyl.[3]—β-Bromonaphthalene in about three times its weight of dry xylene is treated with 5 per cent. of its weight of pure ethyl acetate and a large excess of pasty sodium amalgam. The mixture is gently boiled for thirty hours, cooled, and a large excess of benzene added. After again boiling, the whole is filtered, when mercury di-β-naphthyl crystallises out in glittering scales, M.pt. 238° C. Yield 30 to 35 per cent. The crystals are moderately soluble in boiling hydrocarbons, very slightly soluble in alcohol and ether, and insoluble in water. The compound is completely decomposed when warmed with concentrated mineral acids, forming mercuric salts and substituted naphthalenes. When distilled over soda lime it yields ββ-dinaphthyl. When boiled for one hour with seven parts of arsenious chloride it gives β-naphthylarsenious chloride.[4]

Thiophene Compounds.

Mercury 2 : 2′-dithienyl,[5]



This derivative has been prepared in several ways.

[1] Steinkopf, *Annalen*, 1917, 413, 310.
[2] Kelbe, *Ber.*, 1878, 11, 1503; Michaelis and Schultze, *ibid.*, 1882, 15, 1954.
[3] Michaelis, *Ber.*, 1894, 27, 244; Chattaway, *Trans. Chem. Soc.*, 1894, 65, 877.
[4] Michaelis, *Annalen*, 1902, 320, 342.
[5] Steinkopf and Bauermeister, *Annalen*, 1914, 403, 61.

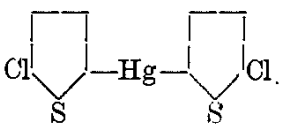
1. Ten grams of 2-chloromercuri thiophene (p. 97) in 150 c.c. of hot xylene are treated with 2 grams of sodium and shaken for thirty minutes, then heated to boiling and filtered. From the filtrate 2·8 grams of mercury dithienyl are obtained on cooling.

2. When 2-chloromercuri thiophene or iodide in acetone is treated with sodium iodide in the same solvent mercury dithienyl results.[1]

3. Mercury dithienyl may also be obtained in 90 per cent. yield by the reduction of 2-chloromercuri thiophene in pyridine-sodium hydroxide solution by means of stannous chloride.[2]

Mercury 2 : 2′-dithienyl crystallises from benzene in pure white crystals, M.pt. 198° to 199° C., insoluble in water, slightly soluble in hot alcohol, readily soluble in benzene or warm chloroform. When its acetone solution is treated with mercuric halides the corresponding 2-halidemercuri thiophenes are obtained. It reacts readily with arsenic trichloride, yielding trithienylarsine, dithienylchloroarsine, and thienyldichloroarsine.

Mercury 5 : 5′-dichloro-2 : 2′-dithienyl,



is formed when an acetone solution of sodium iodide is added to 2-chloromercuri 5-iodothiophene in the same solvent. It crystallises from alcohol in glistening silver crystals, M.pt. 155° C., soluble in acetone or ethyl acetate, in warm benzene or chloroform, and with difficulty in ligroin.

The corresponding 5 : 5′-*dibromo-compound* forms white, matted crystals from benzene, M.pt. 183° C. It readily dissolves in warm benzene or chloroform, but is not very soluble in alcohol.

The 5 : 5′-*di-iodo-derivative* crystallises from a large bulk of hot xylene, in bright yellow needles, 244° to 245° C., only slightly soluble in the usual solvents.

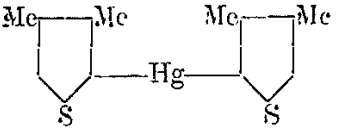
Mercury 5 : 5′-dimethyl-2 : 2′-dithienyl crystallises from alcohol in white needles, melting at 162° to 162·5° C.[3]

Mercury 5 : 5′-di-n-propyl-2 : 2′-dithienyl yields silvery crystals, melting at 57° to 58° C. It is formed from 5-chloromercuri-2-n-propylthiophene by the action of a little more than 2 molecules of sodium iodide in acetone solution. The corresponding *di-isoamyl* compound forms shining crystals from alcohol, melting, not very sharply, at 55° to 57° C.

Mercury 5 : 5′-dibenzyl-2 : 2′-dithienyl.—Four grams of 5-chloromercuri-2-benzylthiophene in 250 c.c. of acetone are mixed with 1·7 grams (2 mols.=1·62 grams) of sodium thiocyanate in 30 c.c. of acetone. The addition of sodium chloride solution precipitates the body (2·3 grams). It is digested with water, dried, and recrystallised from xylene. It melts at 209° to 210° C., previously sintering; is easily soluble in hot toluene, xylene, or pyridine, sparingly in warm benzene and insoluble in alcohol, acetone, or ethyl acetate.

[1] Steinkopf, *Annalen*, 1917, 413, 310.
[2] Steinkopf, *ibid.*, 1923, 430, 71.
[3] Steinkopf, *ibid.*, 1921, 424, 40.

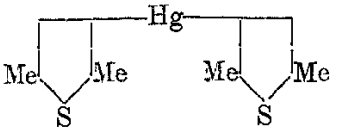
Mercury 3 : 4 : 3′ : 4′-tetramethyl-2 : 2′-dithienyl,



is obtained from 2-iodomercuri-3 : 4-dimethylthiophene in the usual way. It melts at 155° to 156° C. and has similar solubilities to the above compounds.

Mercury 3 : 5 : 3′ : 5′-tetramethyl-2 : 2′-dithienyl crystallises from alcohol in silvery plates, M.pt. 160° to 161° C.

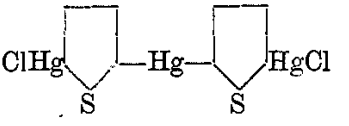
Mercury 2 : 5 : 2′ : 5′-tetramethyl-3 : 3′-dithienyl,



In order to prepare this derivative, sodium is added to a boiling solution of 3-chloromercuri-2 : 5-dimethylthiophene in xylene and the solution filtered whilst hot. The product obtained on cooling is fractionally crystallised from benzene to remove any unchanged starting product. The dithienyl melts at 144° to 145° C.

Mercury 2 : 5 : 2′ : 5′-tetraphenyl-3 : 3′-dithienyl is deposited in prismatic needles from xylene, M.pt. 260° to 261° C.

Mercury-5 : 5′-dichloromercuri-2 : 2′-dithienyl,[1]

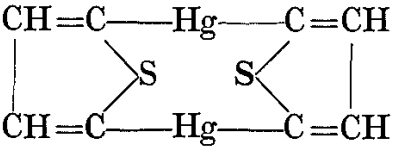


may be prepared as follows :—

Ten grams of 2 : 5-dichloromercuri thiophene in 50 grams of pyridine are heated in an oil-bath. At 70° to 75° C. a flocculent precipitate separates out, and the temperature is raised to 100° C. and maintained for thirty minutes. The product is not quite white, is insoluble in pyridine and the usual solvents, and remains unmelted at 325° C.

A second method of preparation consists in suspending dimercury 2 : 2′ : 5 : 5′-dithienylene in pyridine and treating with mercuric chloride in the same solvent. Yield 35 per cent.

Dimercury 2 : 2′ : 5 : 5′-dithienylene,

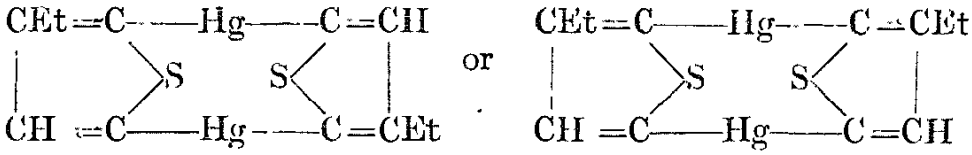


is obtained when 1 gram of 2 : 5-dichloromercuri thiophene in 100 c.c. of pyridine is treated with 0·75 gram (2 mols.) of sodium iodide in 80 c.c. of pyridine. A yield of 0·37 gram (72 per cent.) of substance is obtained. When 4 mols. of sodium iodide are used only a 50 per cent. yield is obtained, and with 2 mols. of sodium thiocyanate only a 24·5

[1] Steinkopf, Bielenberg, and Jensen, *Annalen*, 1923, 430, 71.

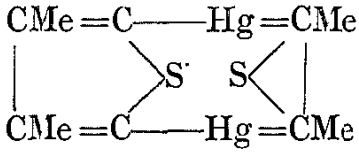
per cent. yield. The body is halogen-free, non-crystalline, and insoluble in pyridine and all the usual solvents. It does not melt at 330° C.

Dimercury 3 : 3′ (or 4′)-diethyl-2 : 2′ : 5 : 5′-dithienylene,



2:5-Dichloromercuri-3-ethylthiophene (2·75 grams) is dissolved in 275 c.c. of pyridine, and with rapid stirring, 3·1 grams (4 mols.) of sodium iodide in 300 c.c. of pyridine added, the stirring being maintained for five and a half hours. Yield 1·43 grams, that is 97 per cent. The product is a yellow powder, blackening at 250° C. and decomposing at 300° to 315° C., and is insoluble in the usual solvents. When treated with 2 mols. of mercuric chloride in pyridine solution at 35° to 45° C. it is converted into **2 : 5-dichloromercuri-3-ethylthiophene.**[1]

Dimercury 3 : 4 : 3′ : 4′-tetramethyl-2 : 2′ : 5 : 5′-dithienylene,



Three grams of 2 : 5 dichloromercuri-3 : 4-dimethylthiophene and 3·3 grams (4 mols.) of sodium iodide in 300 c.c. of pyridine are stirred for two hours. The precipitate is insoluble in all solvents and blackens at 310° C. Yield 1·53 grams (96 per cent.).

DropBooks

Compounds of the Type RHgR′.

Mercury ethyl phenyl.[2]—Phenyl magnesium bromide (23 grams) in absolute ether is treated with ethyl mercuric chloride (9·5 grams) in small portions. After boiling gently, the mixture is allowed to stand for one hour, and then decomposed with 1 per cent. sulphuric acid. The ethereal solution is separated, dried, and evaporated at 40° C. *in vacuo*, when the compound is obtained as an oil. It is fairly soluble in organic solvents, and when kept for several months decomposes into mercury diethyl and mercury diphenyl.

Mercury ethyl benzyl is prepared from ethyl magnesium bromide and benzylmercuric chloride. It is an oil, decomposing on long keeping into mercury diethyl and mercury dibenzyl. When treated with thallic chloride it yields thallous chloride, ethylmercuric chloride, benzylmercuric chloride, and benzaldehyde.[3]

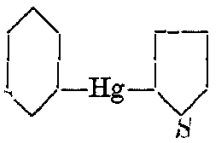
Mercury phenyl benzyl.—To 32 grams of phenyl magnesium bromide (4 mols.) in dry ether, 10·5 grams of finely powdered benzylmercuric chloride are added in small portions, and the mixture worked up as above. A faint yellow oil is obtained, which is freed from

[1] The use of 4 mols. of mercuric chloride gives the same product.
[2] Hilpert and Grüttner, *Ber.*, 1915, 48, 906.
[3] Goddard, *Trans. Chem. Soc.*, 1923, 123, 1168.

impurity by shaking with five times its volume of cold absolute alcohol, and then poured into 200 c.c. of boiling alcohol, and the whole strongly cooled. The oil separates out, and is treated several times with alcohol as above, and finally dried *in vacuo* over phosphorus pentoxide at 35° C. It is slightly soluble in water or cold alcohol, easily in hot alcohol, and miscible with ether, petroleum ether, benzene, and its homologues. At 80° C. it is rapidly decomposed to mercury, dibenzyl, and mercury dibenzyl, whilst at ordinary temperatures it slowly changes to mercury diphenyl and mercury dibenzyl. With faintly acid or neutral solutions of silver nitrate it gives a precipitate immediately, the latter containing no halogen, and when the mixture is boiled silver separates.

Mercury o-tolyl benzyl is a colourless oil, from o-tolyl magnesium bromide and benzylmercuric bromide. It absorbs iodine, yielding benzylmercuric iodide, and when heated at 80° C. for several hours it decomposes into mercury, dibenzyl, and mercury di-o-tolyl.

Mercury phenyl thienyl,[1]



To 7·4 grams of thienyl magnesium bromide in 50 c.c. of ether, 10 grams of phenylmercuric chloride are added in small portions, and a lively reaction ensues giving a clear solution. After completion of the reaction the mass is decomposed with 1 per cent. hydrochloric acid and extracted with ether. From the latter solution 7 grams of faint yellow product are obtained, which on crystallisation from alcohol gives silver-grey plates. Repeated crystallisations give crystals, melting at 163° to 165° C.

Mercury phenyl-p-tolyl.[2]—Kharasch and Marker have recently criticised the preparation of these asymmetrical compounds as practised by Hilpert and Grüttner, on the grounds that the difficulty of obtaining the compounds was due to their use of too large an excess of Grignard reagent, and not controlling the temperature sufficiently. Their modification of Hilpert and Grüttner's method is illustrated by applying it to the preparation of mercury phenyl-p-tolyl, carried out as follows: To two molecular equivalents of phenyl magnesium bromide in dry ether, one molecular equivalent of finely powdered p-tolylmercuric chloride is added in small portions, with constant shaking. The temperature is maintained at 5° C., the shaking continued until all the p-tolyl mercuric chloride dissolves, and the mass decomposed with 0·1 per cent. sulphuric acid, the temperature during the latter operation being kept below 10° C. The product is extracted with ether, the solution dried over anhydrous sodium sulphate, and the solvent removed *in vacuo*. The residue is then washed five times with alcohol and again dried *in vacuo*.

This method is used to prepare the derivatives shown in the following table, and the results of decomposing them with alcoholic hydrogen chloride and alcoholic mercuric chloride are given:—

[1] Steinkopf, *Annalen*, 1923, 430, 70.
[2] Kharasch and Marker, *J. Amer. Chem. Soc.*, 1926, 48, 3130.

Compound.	Products obtained by Decomposition of the Compounds with	
	(1) Alcoholic mercuric chloride.	(2) Alcoholic hydrogen chloride.
Mercury methyl phenyl. (Liq.)	$C_6H_5.HgCl + CH_3.HgCl$.	$CH_3.HgCl$.
Mercury methyl benzyl. (Liq.)	$C_6H_5.CH_2.HgCl + CH_3.HgCl$.	$C_6H_5.CH_2.HgCl$.
Mercury methyl butyl. (Liq.)	$C_4H_9.HgCl + CH_3.HgCl$.	$C_4H_9.HgCl$.
Mercury methyl cyclohexyl. (Liq.)	$C_6H_{11}.HgCl + CH_3.HgCl$.	$C_6H_{11}.HgCl$.
Mercury methyl mesityl. (Solid.)	$(CH_3)_3.C_6H_2.HgCl + CH_3.HgCl$.	$CH_3.HgCl$.
Mercury ethyl naphthyl. (Liq.)	$C_{10}H_7.HgCl + C_2H_5.HgCl$.	$C_2H_5.HgCl + C_{10}H_8$.
Mercury ethyl benzyl. (Liq.)	$C_6H_5.CH_2.HgCl + C_2H_5.HgCl$.	$C_6H_5.CH_2.HgCl + C_2H_5.HgCl$.
Mercury propyl butyl. (Liq.)	$C_3H_7.HgCl + C_4H_9.HgCl$.	$C_3H_7.HgCl + C_4H_9.HgCl$.
Mercury butyl isoamyl.	$C_4H_9.HgCl + C_5H_{11}.HgCl$.	$C_4H_9.HgCl + C_5H_{11}.HgCl$.
Mercury butyl phenyl. (Liq.)	$C_4H_9.HgCl + C_6H_5.HgCl$.	$C_4H_9.HgCl$.
Mercury phenyl cyclohexyl. (Solid.)	$C_6H_{11}.HgCl + C_6H_5.HgCl$.	$C_6H_{11}.HgCl$.
Mercury phenyl naphthyl. (Solid.)	$C_{10}H_7.HgCl + C_6H_5.HgCl$.	$C_6H_5.HgCl + C_{10}H_8$.
Mercury phenyl o-anisyl. (Solid.)	$o\text{-}C_6H_4(OCH_3).HgCl + C_6H_5.HgCl$.	$C_6H_5.HgCl$.
Mercury phenyl mesityl. (Solid.)	$(CH_3)_3.C_6H_2.HgCl + C_6H_5.HgCl$.	$C_6H_5.HgCl$.
Mercury phenyl p-tolyl. (Solid.)	$CH_3.C_6H_4.HgCl + C_6H_5.HgCl$.	$C_6H_5.HgCl$.

Compounds of the Type RHgX.

Phenylmercuric Compounds.

Phenylmercuric chloride, C_6H_5HgCl.—This substance is obtained in several ways :

1. A 94 per cent. yield may be obtained from mercury diphenyl under the following conditions : 2·5 grams of the latter substance in 25 c.c. of acetone are treated with 1·95 grams of mercuric chloride in 10 c.c. of acetone, when phenylmercuric chloride (3·7 grams) is immediately precipitated. A further 0·5 gram may be recovered from the filtrate by the addition of water.[1] A similar reaction takes place in alcohol.

2. A large number of substances react with mercury diphenyl, giving phenylmercuric chloride as one of the products of reaction, the yield in some cases being very small. The following list gives the most important of these reagents :—

Dry chlorine gas,[2] hypochlorous acid,[2] thallic chloride,[3] silicon tetrachloride,[4] stannic chloride,[5] zirconium tetrachloride,[6] phosphorus trichloride,[7] mercurous chloride,[8] thionyl chloride,[9] benzene sulphonic chloride,[10] benzal chloride,[11] phenyl iododichloride.[12]

[1] Steinkopf, *Annalen*, 1917, 413, 329.
[2] Dreher and Otto, *Annalen*, 1870, 154, 93.
[3] Goddard, *Trans. Chem. Soc.*, 1922, 121, 40.
[4] Ladenburg, *Annalen*, 1874, 173, 152.
[5] Aronheim, *Annalen*, 1878, 194, 148.
[6] Peters, *Ber.*, 1908, 41, 3173.
[7] Schwarze, *J. prakt. Chem.*, 1874, 10, [2], 222 ; Michaelis and Graeff, *Ber.*, 1875, 8, 922 ; Michaelis, *Annalen*, 1876, 181, 290.
[8] Otto, *J. prakt. Chem.*, 1870, 1, [2], 179.
[9] Heumann and Köchlin, *Ber.*, 1883, 16, 1625.
[10] Otto, *Ber.*, 1885, 18, 246.
[11] Kekulé and Franchimont, *Ber.*, 1872, 5, 906.
[12] Willgerodt, *Ber.*, 1898, 31, 915.

DropBooks

3. From benzene.[1] A mixture of 50 grams of mercuric acetate, 50 c.c. of glacial acetic acid, and 100 c.c. of thiophene-free benzene is heated in a pressure flask for five hours at 100° C., then cooled, the residue filtered off and washed several times with benzene. The filtrate which contains the acetate is evaporated down and treated with alcoholic calcium chloride solution, when the chloride is precipitated. This is filtered off and washed with hot water to remove any adhering calcium chloride.

4. From benzene sulphinic acid.[2] This acid in dilute alcohol is treated with an aqueous solution of mercuric chloride and the whole heated until the evolution of sulphur dioxide ceases. The solid product thus obtained is found to contain small quantities of phenylmercuric chloride.

5. By heating phenyl boric acid with aqueous mercuric chloride solution.[3]

6. By heating triphenylstibine with 3 mols. of mercuric chloride, when antimony trichloride and 3 mols. of phenylmercuric chloride are formed.[4]

7. Phenylmercury 2 : 4 : 6-trinitrophenyl is boiled with mercuric chloride in alcoholic solution, phenylmercuric chloride and trinitrophenylmercuric chloride being formed.[5]

Phenylmercuric chloride crystallises from a large quantity of hot benzene in satin plates, melting at 250° to 251° C., insoluble in water, and only slightly soluble in cold alcohol or benzene. It readily sublimes without decomposition on gently heating.

Treatment with moist silver oxide gives a solution of the corresponding hydroxide ; dry silver oxide does not yield an oxide but decomposes the chloride with formation of mercury diphenyl, mercuric oxide, and silver chloride.[6] When an acetone solution of phenylmercuric chloride is treated with a similar solution of sodium iodide, phenylmercuric iodide is formed.[7] Arsenic trichloride heated at 100° C. for four to five hours with the chloride yields phenyl dichloroarsine.[8] With phenyl iododichloride it yields mercuric chloride and diphenyl iodonium chloride.[9] Ethyl mercaptan decomposes phenylmercuric chloride at 150° C., yielding *ethyl thio-mercuric chloride,* ClHg.SEt.[10]

Phenylmercuric bromide may be obtained from phenyl magnesium bromide and mercuric bromide in dry ether ; [11] by the interaction of mercury diphenyl and two atoms of bromine ; if four atoms of the halogen are used, bromobenzene and mercuric bromide result.[12] When mercury diphenyl and mercuric bromide in alcoholic solution are heated at 120° C., and when ethylene dibromide and mercury diphenyl are heated at 200° C. this bromide is also formed.

The bromide crystallises in a similar form to the chloride, and melts

[1] Roeder and Blasi, *Ber.*, 1914, 47, 2751.
[2] Peters, *Ber.*, 1905, 38, 2567.
[3] Michaelis and Becker, *Ber.*, 1882, 15, 182.
[4] Michaelis and Reese, *Annalen*, 1886, 233, 49.
[5] Kharasch and Grafflin, *J. Amer. Chem. Soc.*, 1925, 47, 1948.
[6] Otto, *J. prakt. Chem.*, 1870, 1, [2], 184.
[7] Steinkopf, *Annalen*, 1917, 413, 329.
[8] Roeder and Blasi, *loc. cit.*
[9] Willgerodt, *Ber.*, 1898, 31, 915.
[10] Sachs, *Ber.*, 1920, 53, 1737.
[11] Hilpert and Grüttner, *Ber.*, 1913, 46, 1686.
[12] Dreher and Otto, *Annalen*, 1870, 154, 93.

at 276° C.; it resembles the chloride in its solubility and general properties. An alcoholic solution of potassium sulphide on prolonged boiling with the bromide gives mercury diphenyl, mercuric sulphide, and potassium bromide.

Phenylmercuric iodide may be obtained as follows :—

1. From phenylmercuric chloride and sodium iodide, the reaction being carried out in acetone. Yield 77·5 per cent.[1]

2. Mercury diphenyl in alcohol or carbon bisulphide is treated with a solution of iodine in the same solvent.[2] A similar result is obtained if mercuric iodide replaces the iodine and the whole is boiled.

3. Phenylmercuric cyanide is decomposed by iodine, yielding the iodide.[3]

The iodide crystallises in glistening satin plates, melting at 264° to 266° C. The crystals are odourless, not affected by light, insoluble in water, very slightly soluble in cold alcohol, ether, benzene, readily soluble in chloroform or hot benzene. When heated above its melting-point phenylmercuric iodide gives mercuric iodide.

When an alcoholic or carbon bisulphide solution of the iodide is treated with iodine, iodobenzene and mercuric iodide result, but sodium iodide does not react with an acetone solution of the iodide.[4] Sodium amalgam reacts with an alcoholic solution of phenylmercuric iodide giving mercury, mercury diphenyl, and hydrogen iodide, but if the reaction be carried out in dry benzene, mercury, mercury diphenyl, and sodium iodide are obtained.[5]

Phenylmercuric thiocyanate, $C_6H_5Hg.CNS$.[6]—This compound was first obtained by heating together equal molecules of mercury diphenyl and mercury thiocyanate, and later by treating phenylmercuric iodide with free thiocyanogen in carbon bisulphide solution. It has more recently been formed by treating phenyl mercuric chloride with sodium thiocyanate in acetone solution, or boiling mercury diphenyl with mercury thiocyanate in acetone solution.[7] It crystallises in small, pearly plates, melting at 231° to 232·5° C., insoluble in water, soluble in boiling alcohol or benzene.[8]

Phenylmercuric cyanide.[9]—When an equal number of molecules of mercury diphenyl and mercuric cyanide in alcoholic solution are heated in a sealed tube at 120° C. the cyanide is formed. It is also obtained when the corresponding iodide is treated with silver cyanide. From benzene it crystallises in large rhombic plates, melting at 203° to 204° C., somewhat soluble in boiling water, easily in boiling alcohol. Heated in a sealed tube at 120° C. with concentrated hydrochloric acid it gives benzene, mercuric chloride, formic acid, and ammonium chloride; heated with potassium hydroxide it yields mercury, benzene, and potassium cyanate. It is decomposed by iodine, with formation of phenylmercuric iodide and cyanogen iodide, and by hydrogen sulphide yielding benzene, mercuric sulphide, and hydrogen cyanide.

Phenylmercuric hydroxide.—Solutions of this body are obtained

[1] Steinkopf, *Annalen*, 1917, 413, 329.
[2] Dreher and Otto, *loc. cit.*
[3] Otto, *J. prakt. Chem.*, 1870, 1, [2], 182.
[4] Steinkopf, *loc. cit.*
[5] Dreher and Otto, *loc. cit.*
[6] Otto, *J. prakt. Chem.*, 1870, 1, [2], 182; Söderbäck, *Annalen*, 1919, 419, 266.
[7] Steinkopf, *Annalen*, 1921, 424, 60.
[8] For the type R′.Hg.S.R″, see Sachs, *Annalen*, 1923, 433, 154.
[9] Otto, *loc. cit.*

when mercury diphenyl is oxidised by potassium permanganate,[1] or when the corresponding halides are treated with moist silver oxide. The components are boiled in alcohol, then evaporated *in vacuo*, when small, white rhombic prisms are deposited, sintering at 160° C. and melting above 200° C. The crystals are slightly soluble in cold water, more soluble in alcohol or benzene. The aqueous solution liberates ammonia from its salts, and precipitates alumina from aluminium salts. Treatment with acids yields the corresponding salts.

Phenylmercuric nitrate.—Alcoholic solutions of the chloride on long boiling with silver nitrate yield the nitrate in shining, rhombic plates, melting at 165° to 168° C. with decomposition, somewhat soluble in boiling water, easily soluble in boiling alcohol or benzene. Treatment with concentrated nitric acid gives benzene and mercuric nitrate. Mercury diphenyl when treated with mercuric nitrate or nitrogen trioxide or tetroxide also yields phenylmercuric nitrate.[2]

Phenylmercuric carbonate[3] is prepared from the chloride in a similar manner to the nitrate using silver carbonate. It forms small, white needles, very slightly soluble in boiling water, easily soluble in boiling alcohol or benzene. When heated it melts with decomposition, and with strong acids gives carbon dioxide and the corresponding salts.

Phenylmercuric formate.[4]—When mercury diphenyl and formic acid are boiled for a short time, then poured into water, the formate is precipitated. It crystallises from hot formic acid in glistening plates, M.pt. 171° C.

Phenylmercuric acetate may be prepared as follows :—

1. A mixture of 80 c.c. of benzene, 15 grams of mercuric acetate, and 20 c.c. of 95 per cent. alcohol are heated at 100° C. for five hours. A yellow precipitate forms during this time which is dissolved by the addition of a few c.c. of glacial acetic acid. A further 20 c.c. of alcohol are now added and the heating continued for a further fifty hours. The solution is then filtered, evaporated to dryness, and the residue recrystallised from 95 per cent. alcohol. Yield 12·6 grams (80 per cent.).[5]

2. By boiling a mixture of mercury diphenyl and glacial acetic acid.

3. By heating mercury diphenyl and mercuric acetate in alcoholic solution in a sealed tube for one hour at 120° C.[6]

4. By heating phenylmercuric iodide and silver acetate for a long time in dilute spirit.

5. By boiling benzene for several hours at 110° C. with dry mercuric acetate.[7] The acetate crystallises in small, white, odourless, glistening, oblique, rhombic prisms, M.pt. 149° C., easily soluble in hot water, glacial acetic acid, benzene, or alcohol.

When heated at 150° C. phenylmercuric acetate gives carbon, benzene, mercury, oxygen, and acetic anhydride. Dry distillation yields mercury, diphenyl oxide, and acetic anhydride. Distillation with sulphur gives mercury, benzene, acetic acid, acetic anhydride, and diphenyl sulphide. Boiling with dilute sulphuric or hydrochloric acid produces benzene, acetic acid, and a mercuric salt. The acetate is reduced by nascent hydrogen to benzene, mercury, and acetic acid.

[1] Otto, *J. prakt. Chem.*, 1884, [2], 29, 136.
[2] Bamberger, *Ber.*, 1897, 30, 506.
[3] Otto, *loc. cit.*
[4] Dreher and Otto, *Annalen*, 1870, 154, 93.
[5] Maynard, *J. Amer. Chem. Soc.*, 1924, 46, 1511.
[6] Otto, *loc. cit.*
[7] Dimroth, *Ber.*, 1898, 31, 2154; 1899, 32, 758.

Treated with iodine, a warm aqueous solution yields iodobenzene, acetic acid, and mercuric iodide. Aqueous or alcoholic hydrogen sulphide gives a heavy white precipitate, which turns gray and then black, the resulting solution containing benzene, acetic acid, and mercuric sulphide. Heated with yellow ammonium sulphide at 100° to 110° C. in sealed tubes gives a similar result to the preceding. Heating with arsenic trichloride for four to five hours at 100° C., gives phenyldichloroarsine.[1]

Reduction by alkaline sodium stannite gives mercury diphenyl in 95·6 per cent. yield.[2]

Phenylmercuric propionate, prepared in the same way as the formate, forms matted crystals, sintering at 145° C. and melting at 165° to 166° C. It may be recrystallised from water, and is also soluble in alcohol or benzene.

Phenylmercuric myristate.[3]—Equal numbers of molecules of myristic acid and mercury diphenyl are heated together in alcoholic solution in a sealed tube at 120° C. Small, fatty, rhombic scales are obtained, insoluble in water, soluble in boiling alcohol or benzene, and when boiled with hydrochloric acid they are decomposed into benzene, myristic acid, and mercuric chloride.

Phenylmercuric sulphide.[4]—Phenylmercuric acetate is dissolved in ammonium hydroxide—ammonium acetate solution, and treated with hydrogen sulphide or an alkali sulphide, when phenylmercuric sulphide is precipitated as a white amorphous powder. It is insoluble in water or alcohol but dissolves in chloroform, this solution soon decomposing. Hydrochloric acid liberates hydrogen sulphide, and continued boiling with alcohol gives mercuric sulphide and mercury diphenyl. Heated to 108° C. the compound blackens and decomposes.

Phenylmercuric thiocarbonate, $(C_6H_5Hg)_2CS_3$.—When the above sulphide is dissolved in cold carbon bisulphide the solution first deposits silky needles, and afterwards a yellow product which is only slightly soluble in carbon bisulphide. This substance is the thiocarbonate, which is insoluble in water or alcohol, slightly soluble in ether or benzene, more soluble in chloroform, and forms a clear solution in hot fuming hydrochloric acid. At 108° C. it blackens, mercuric sulphide being deposited and carbon disulphide evolved. It is rapidly decomposed when heated with benzene, with the production of mercury diphenyl and mercuric sulphide.

Phenylmercuric thiosulphate.[5]—Two molecules of phenylmercuric acetate in ammonium hydroxide—ammonium acetate solution are treated with one molecule of sodium thiosulphate, when a white precipitate is obtained, insoluble in ordinary solvents but dissolving in concentrated hydrochloric acid, with evolution of sulphur dioxide and deposition of sulphur. This thiosulphate readily dissolves in aqueous sodium thiosulphate, the solution giving mercury diphenyl on standing. The compound is not decomposed when heated to 200° C.

Compounds of Di(phenylmercuri)-amine, $(C_6H_5Hg)_2NH$.[6]

Pesci has shown that phenylmercuric salts react with ammonia to form salts of $(C_6H_5Hg)_2NH$—, these compounds yielding ammonia

[1] Roeder and Blasi, *Ber.*, 1914, 47, 2752.
[2] Maynard, *J. Amer. Chem. Soc.*, 1924, 46, 1511; Dimroth, *Ber.*, 1902, 35, 2853.
[3] Otto, *J. prakt. Chem.*, 1870, 1, [2], 185.
[4] Pesci, *Gazzetta*, 1899, 29, 1. 394. [5] Pesci, *ibid.* [6] Pesci, *ibid.*, 1909, 39, 1. 147.

when decomposed, but no hydroxide when treated with alkalies or silver hydroxide.

Phenylmercuriamine acetate, $(C_6H_5Hg)_2NH_2.O.CO.CH_3$.—This compound separates out when phenylmercuric acetate is dissolved in ammonium hydroxide. It crystallises from methyl alcohol in needles, melting at 179° C., readily soluble in alcohol, sparingly soluble in water. Excess of concentrated sodium thiosulphate or refluxing with alcoholic carbon bisulphide gives mercury diphenyl.

The *nitrate* is formed when ammonium nitrate is added to the above ammoniacal solution of phenylmercuric acetate. It forms brilliant scales from alcohol, melting at 230° to 235° C. with decomposition.

The *sulphate* is precipitated by sodium sulphate and is an infusible precipitate, forming a compound with ammonium sulphate,

$$[(C_6H_5Hg)_2NH_2]_2SO_4.(NH_4)_2SO_4$$

which crystallises in rectangular tablets.

The *chloride*, prepared from phenylmercuric chloride, crystallises in microscopic prisms, melting at 184° C. with decomposition.

Tetra (phenylmercuri) thiourea, $(C_6H_5Hg)_4N_2CS$.—The above acetate treated with thiourea gives this derivative and ammonium acetate. It is insoluble in the usual solvents and darkens at 104° to 105° C. When boiled with alcohol it decomposes, giving mercuric sulphide, mercury diphenyl, and phenylmercuri cyanamide,

$$(C_6H_5Hg)_4N_2CS = HgS + (C_6H_5)_2Hg + (C_6H_5Hg)_2N-CN$$

Phenylmercuri cyanamide, formed as shown above, is a white amorphous powder which decomposes when heated. It is decomposed by cold dilute hydrochloric acid into phenylmercuric chloride and cyanamide.

Tolylmercuric Compounds.

o-Tolylmercuric chloride may be prepared by treating o-tolyl boric acid with mercuric chloride,[1] or by separating it from the para compound formed when toluene is mercurated by mercuric acetate after treating the mixture with sodium chloride.[2] It crystallises from alcohol in white crystals, M.pt. 146° C.[3]

o-Tolylmercuric bromide.[4]—To a solution of 28 grams of o-tolyl magnesium bromide in 100 grams of ether, 58 grams of mercuric bromide are added, the mixture shaken for one hour, boiled for two hours, and then allowed to stand over-night. It is then worked up in the usual way, when 42 grams (78 per cent. yield) of the bromide are obtained. From xylene or alcohol it forms hair-fine needles, M.pt. 168° C., easily soluble in pyridine or aniline and reprecipitated by the addition of petroleum ether. It is only slightly soluble in cold alcohol, ether, benzene, chloroform, or acetone, but readily soluble in hot benzene or its homologues. The crystals are not affected by light.

o-Tolylmercuric iodide.—When the above bromide is boiled with alcoholic potassium iodide in slight excess, a quantitative yield of the

[1] Michaelis, *Ber.*, 1894, 27, 244.
[2] Dimroth, *Ber.*, 1899, 32, 758.
[3] Coffey, *Trans. Chem. Soc.*, 1925, 127, 1029.
[4] Hilpert and Grüttner, *Ber.*, 1915, 48, 906.

iodide is obtained. It crystallises in prisms from alcohol, melting at 176° to 177·5° C., and has a similar solubility to the bromide.

o-Tolylmercuric sulphide.—When hydrogen sulphide is passed into a pyridine-ether solution of the above iodide at −10° C., the pale yellow sulphide is precipitated. In the presence of moisture it soon decomposes and blackens, mercuric sulphide separating out.

o-Tolylmercuric nitrate is formed when mercury di-o-tolyl is treated with nitrogen trioxide or tetroxide.[1]

m-Tolylmercuric chloride[2] is readily obtained from m-tolyl boric acid, as in case of the ortho compound;[3] from tri-m-tolylstibine mercurichloride by boiling with alcohol;[4] and by heating an alcoholic solution of mercury di-m-tolyl with mercuric chloride.

It crystallises in white needles, melting at 159° to 160° C., easily soluble in chloroform or benzene, with difficulty in alcohol, and it sublimes without decomposition.

The *bromide* is prepared in the same way as the chloride; it crystallises from alcohol in white needles, M.pt. 183° to 184° C.

The *iodide* forms white pearly plates, M.pt. 161° to 162° C.; the *acetate*, white shining needles from water, M.pt. 83° to 84° C.; the *formate*, large needles, M.pt. 106° C.; the *propionate*, white needles, M.pt. 102° C., insoluble in cold water, easily soluble in alcohol.

p-Tolylmercuric chloride.—This derivative is prepared as follows:—

1. A mixture of 300 c.c. of water and 100 grams of powdered mercuric chloride is heated in a 2-litre beaker, and a solution of 80 grams of sodium p-toluene sulphinate in 200 c.c. of boiling water carefully added to the hot solution. A heavy white precipitate is thrown down and sulphur dioxide is evolved. When the frothing ceases, 200 c.c. of water are added, and the mixture boiled, with occasional stirring, until the evolution of sulphur dioxide slackens. A further 200 c.c. of water are now added and boiling continued until no more sulphur dioxide is given off. The mixture is filtered, and washed with water until the washings give no precipitate with sodium hydroxide, the residue then being dried at 110° C. Yield 65 per cent.[5]

2. Heating p-tolyl sulphinic acid with mercuric chloride until evolution of sulphur dioxide ceases.[6]

3. Heating p-tolyl sulphonyl chloride with mercury diphenyl for fifteen hours at 120° C.[7]

4. By heating mercuric chloride and mercury di-p-tolyl in alcoholic solution in a sealed tube at 160° C.[8]

5. From p-tolyl boric acid in the usual way.[9]

6. By separation of the ortho and para isomers formed in the direct mercuration of toluene by mercuric acetate, after treating with sodium chloride.[10]

[1] Kunz, *Ber.*, 1898, 31, 1528.
[2] Michaelis, *Ber.*, 1895, 28, 588.
[3] Khotinsky and Melamed, *Ber.*, 1909, 42, 3094.
[4] Michaelis and Genzken, *Annalen*, 1887, 242, 176.
[5] Whitmore, Hamilton, and Thurman, *J. Amer. Chem. Soc.*, 1923, 45. 1066.
[6] Peters, *Ber.*, 1905, 38, 2569.
[7] Otto, *Ber.*, 1885, 18, 246.
[8] Otto, *J. prakt. Chem.*, 1870, 1, [2], 185.
[9] Michaelis and Becker, *Ber.*, 1882, 15, 185.
[10] Dimroth, *Ber.*, 1899, 32, 758; *cf.* Coffey, *Trans. Chem. Soc.*, 1925, 127, 1029.

The chloride crystallises in shining scales, melting at 232° to 233° C.; it is insoluble in water, soluble with difficulty in hot alcohol and easily in boiling benzene. Its solution in acetone when treated with sodium iodide yields p-tolylmercuric iodide, but no mercury di-p-tolyl is formed.[1]

p-Tolylmercuric bromide.—From 28 grams of p-tolyl magnesium bromide and 58 grams of mercuric bromide a yield of 44 grams of p-tolylmercuric bromide is obtained.[2] The yield is not so good when mercuric chloride is used in place of the bromide.[3]

The bromide crystallises in fine needles from benzene, melting at 234° to 235° C. It is sparingly soluble in the usual organic solvents. It reacts with phosphenyl chloride in two to three hours at 270° C. in dry carbon dioxide to form phenyl-p-tolylchlorophosphine.

p-Tolylmercuric iodide.—This derivative may be prepared from the chloride as shown above, or from the bromide by boiling with potassium iodide in alcoholic solution for two hours. Its melting-point has been given as 213° to 214° C. and 217° C.; it is sparingly soluble in organic solvents.[4]

p-Tolylmercuric carbonate is a crystalline powder, decomposing above 260° C.

p-Tolylmercuric mercaptan is a yellow, insoluble product prepared from the above carbonate and carbon disulphide.

p-Tolylmercuric nitrate is prepared similarly to the ortho compound from mercury di-p-tolyl and trioxide or tetroxide of nitrogen.[5]

p-Tolylmercuric acetate.—The methods of preparation of this derivative, as also of the preceding one, are similar to those for the phenyl compound. It forms rhombic prisms from alcohol and benzene, M.pt. 153° C. It is less soluble in the usual solvents than the phenyl compound.

p-Tolylmercuric-2 : 4 : 6-trinitrobenzoate is prepared from the hydroxide and the substituted benzoic acid in alcoholic solution. It melts at 227° C., but when heated in an oil-bath at 220° to 230° C. until all effervescence ceases it forms **p-tolylmercuric-2 : 4 : 6-trinitrophenyl**, a pale yellow product, M.pt. 192° C.[6]

Benzylmercuric Compounds.

Benzylmercuric chloride[7] is obtained as follows :—

1. To a solution of 23·8 grams of benzyl magnesium chloride in 100 grams of ether, 46·7 grams (1·1 mols.) of finely powdered mercuric chloride are slowly added with good shaking. Until the reaction is finished, the temperature is maintained below 45° C., and the reaction mixture then allowed to stand for twenty-four hours. It is then boiled briskly for two hours, decomposed by ice and dilute sulphuric acid, filtered and washed with water, not exceeding 80° C. The residue is then recrystallised from equal parts of xylene and alcohol. Yield 43 grams (84 per cent.).

[1] Steinkopf, *Annalen*, 1917, 413, 329.
[2] Hilpert and Grüttner, *Ber.*, 1915, 48, 906.
[3] Pope and Gibson, *Trans. Chem. Soc.*, 1912, 101, 735.
[4] Steinkopf, *loc. cit.*; Hilpert and Grüttner, *loc. cit.*
[5] Kunz, *Ber.*, 1898, 31, 1528.
[6] Koten and Adams, *J. Amer. Chem. Soc.*, 1924, 46, 2768.
[7] Hilpert and Grüttner, *Ber.*, 1915, 48, 913.

2. From benzyl boric acid and mercuric chloride.[1]

3. From mercury dibenzyl and an alcoholic solution of mercuric chloride.

The chloride crystallises in white, glistening plates, M.pt. 104° C., and decomposes when strongly heated. It reacts with benzyl magnesium chloride to form mercury dibenzyl.[2]

The corresponding *bromide* and *iodide* may be prepared by Method 3, the former giving plates melting at 119° C., and the latter plates, M.pt. 117° C.[3]

The *cyanide* is formed when mercury dibenzyl and mercuric cyanide in absolute alcoholic solution are heated at 130° C. in a sealed tube. It crystallises in fine, white needles, M.pt. 124° C.

The *acetate* results when mercury dibenzyl in alcoholic solution is treated with mercuric acetate; and when silver acetate is added to an alcoholic solution of benzylmercuric chloride.

It forms long, glistening, white needles, melting at 126° C.

Compounds from Higher Benzene Homologues.

m-Xylylmercuric chloride is obtained, along with m-xylyldichlorophosphine, when mercury di-m-xylyl is heated at 230° C. with phosphorus trichloride.[4]

Mesitylmercuric chloride occurs as fine needles, melting about 200° C.; the *bromide* melts at 194° C.; the *iodide* yields fine, colourless needles, melting about 178° C.[5]

Pseudocumylmercuric chloride yields small needles, M.pt. 201° C.; the *bromide* is a white micro-crystalline powder, M.pt. 211° C.; the *iodide*, formed by heating mercury dipseudocumyl with excess of mercuric iodide in a sealed tube at 130° to 140° C. in alcoholic solution, crystallises as white glistening needles, M.pt. 196° to 197° C.

Cumylmercuric chloride (glistening needles, M.pt. 156° C.); *bromide* (M.pt. 163° C.); and *iodide* (M.pt. 169° C.)[6] are also known.

Cyclohexyl Compounds.[7]

Cyclohexylmercuric chloride is formed by the action of mercuric chloride on mercury dicyclohexyl in any solvent, and all the following salts may be prepared in a similar manner. The chloride crystallises in plates of brilliant lustre, M.pt. 163° to 164° C., and may be converted to the *iodide* by warming its solutions with potassium iodide.

The *bromide* crystallises from benzene in white leaflets, M.pt. 153° C., 100 grams of benzene dissolving 3·33 grams of bromide at 29° C. It is insoluble in water, more soluble in ether or benzene, very soluble in amines or pyridine. It is sensitive to light.[8]

[1] Khotinsky and Melamed, *Ber.*, 1909, 42, 3095.
[2] Jones and Werner, *J. Amer. Chem. Soc.*, 1918, 40, 1257.
[3] Wolff, *Ber.*, 1913, 46, 64.
[4] Weller, *Ber.*, 1887, 20, 1718.
[5] Michaelis, *Ber.*, 1895, 28, 588.
[6] Michaelis, *ibid.*; Schiff, *Ber.*, 1877, 10, 1745.
[7] Grüttner, *Ber.*, 1914, 47, 1651; Tiffeneau and Gannagé, *Bull. Sci. Pharmacol.*, 1921, 28, 7.
[8] Tiffeneau and Gannagé give chloride, M.pt. 159° C.; bromide, M.pt. 141° C.; iodide, M.pt. 142° C.

The *iodide* may be obtained from the chloride or bromide by the action of potassium iodide, or by treating cyclohexyl iodide with sodium amalgam.[1] It has a similar solubility to the bromide, is sensitive to light, and crystallises in plates, M.pt. 143° C.

Treatment of the above halides with silver oxide yields the *hydroxide*, a strong base, which decomposes when heated.

The *sulphide* is a pure white powder, deposited when a rapid stream of hydrogen sulphide is passed into a pyridine solution of the bromide at −10° C. If left in a moist state it soon decomposes.

The *cyanide* crystallises from alcohol in sparkling leaflets, melting at 144° C., and is sensitive to light.

4-Methylcyclohexylmercuric chloride forms spangles, subliming at 163° C.; the *bromide* has M.pt. 142° C., *iodide*, M.pt. 176° C., *cyanide*, M.pt. 100° C., and *hydroxide*, M.pt. 110° to 115° C.[2] are also known.

Naphthyl Compounds.

α-Naphthylmercuric chloride is prepared by boiling an acetone or alcoholic solution of mercury di-α-naphthyl with mercuric chloride, filtering, and precipitating the chloride with water.[3] It crystallises in quadratic plates, M.pt. 188° to 189° C., and its acetone solution with sodium iodide yields the corresponding iodide. It is moderately soluble in alcohol or benzene, but insoluble in water.[4]

α-Naphthylmercuric bromide may be prepared from mercury di-α-naphthyl either by the action of bromine, or by heating it with mercuric bromide in alcoholic solution for one hour at 120° to 130° C.[5] Naphthyl magnesium bromide and mercuric bromide give the same product.[6] The compound crystallises in glistening needles or plates, M.pt. 202° C., insoluble in water, easily soluble in alcohol, chloroform, benzene, or carbon bisulphide.

α-Naphthylmercuric iodide crystallises in rhombic columns, M.pt. 185·5° to 186° C., and is obtained from the chloride as described above, or from mercury di-α-naphthyl by the action of iodine in carbon bisulphide solution. It is insoluble in water, slightly soluble in cold alcohol or ether, easily soluble in hot alcohol, chloroform, benzene, or carbon bisulphide. When strongly heated it decomposes with separation of carbon, and heated with soda lime yields mercuric oxide, iodine, and naphthalene. Its alcoholic solution treated with sodium amalgam gives mercury, hydrogen iodide, and mercury di-α-naphthyl.[7]

α-Naphthylmercuric acetate is prepared as follows :—

1. Mercury di-α-naphthyl is treated with an excess of glacial acetic acid and the mixture heated until complete solution is obtained, then the whole poured into water. The precipitate, which contains the acetate and naphthalene, is filtered off and washed with water, then crystallised from hot alcohol, in which the naphthalene is less soluble than the acetate.

[1] Kursanov, *Chem. Zentr.*, 1899, II. 477.
[2] Tiffeneau and Gannagé, *Bull. Sci. Pharmacol.*, 1921, 28, 7.
[3] Steinkopf, *Annalen*, 1917, 413, 330; see Matsumiya, *Mem. Coll. Sci. Kyōtō*, 1925, 8, 391.
[4] Otto, *J. prakt. Chem.*, 1870, [2], 1, 185.
[5] Otto, *Annalen*, 1870, 154, 188.
[6] Hilpert and Grüttner, *Ber*, 1913, 46, 1686.
[7] Otto, *loc. cit.*; Otto and Morjes, *Annalen*, 1868, 147, 164.

2.[1] Thirty grams of pure dry mercuric acetate are introduced into 60 grams of molten naphthalene, the mixture well stirred and heated to 120° C., this temperature being maintained until a clear solution results (about twenty minutes). The excess of naphthalene is then removed by steam and the dry residue extracted with ligroin, from which the product crystallises on cooling. If the reaction product before steam distillation is treated with sodium chloride, the chloride is obtained instead of the acetate.

The acetate crystallises from alcohol in colourless needles, M.pt. 154° C., which are insoluble in water, slightly soluble in ether, and easily soluble in hot glacial acetic acid, alcohol, benzene, chloroform, or carbon bisulphide.

It reacts with hydrochloric or hydriodic acids, giving acetic acid, naphthalene, and a mercuric halide; four atoms of iodine react giving acetic acid, mercuric iodide, and iodonaphthalene; sodium amalgam on the alcoholic solution yields mercury, acetic acid, and naphthalene; alcoholic hydrogen sulphide or ammonium sulphide at 100° C. break the compound down into acetic acid, mercuric sulphide, and naphthalene.

The *formate* is an oil, and the *butyrate* forms fine, glistening, rhombic prisms, melting about 200° C., almost insoluble in cold water, moderately soluble in hot water, alcohol, or butyric acid.

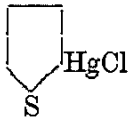
The *nitrate* is prepared by the interaction of silver nitrate and α-naphthylmercuric chloride in alcoholic solution,[2] or from mercury di-α-naphthyl and nitrogen trioxide. It crystallises in small white needles.

The *thiocyanate* occurs as white plates, soluble in hot alcohol or benzene; the *sulphide* has only been obtained as a white precipitate.

DropBooks

Thienyl Compounds.

2-Chloromercuri thiophene,



In order to prepare this derivative, 10 parts of thiophene in 100 parts of spirit are mixed with 1000 parts of a cold saturated solution of mercuric chloride and 200 parts of a 33⅓ per cent. solution of crystallised sodium acetate. In four or five days the precipitate is filtered off and the filtrate deposits further crystals. The residue is washed with cold water, boiled with spirit, and filtered through a hot-water funnel, the chloride crystallising out on cooling.[3]

The above method of preparation yields a mono- and a di-mercurated thiophene; the latter is very insoluble in the usual solvents, so that the mono-compound is removed by means of hot alcohol.[4] 2-Chloromercuri

[1] Dimroth, *Ber.*, 1902, 35, 2032.

[2] Otto, *J. prakt. Chem.*, 1870, [2], 1, 185.

[3] Volhard, *Annalen*, 1891, 267, 176; Steinkopf and Bauermeister, *Annalen*, 1914, 403. 59; Finzi, *Gazzetta*, 1915, 45, ii. 280; Steinkopf, *Annalen*, 1921, 424, 23.

[4] From 85 grams of thiophene Steinkopf obtained in six days 217 grams of mono-compound and 18 grams of di-compound, but the author finds that a considerable increase in yield may be obtained if the liquors be allowed to stand for six months after the first batch of crystals has been removed. It may also be prepared by treating mercury 2 : 2'-thienyl in acetone solution with mercuric chloride. Yield 89·4 per cent.

thiophene crystallises in white, silvery plates, M.pt. 183° C., somewhat volatile, commencing to sublime above 100° C., subliming rapidly at 210° C.; in large quantities this process is accompanied by decomposition. With sodium iodide in acetone solution it yields mercury 2 : 2′-dithienyl and the corresponding iodide. With mercuric bromide or iodide the corresponding 2-halidemercuri thiophenes are obtained.[1]

When boiled with arsenic trichloride in toluene for six to seven hours dithienylchloroarsine and thienyldichloroarsine[2] are obtained.

Thienones are formed by heating the chloride with the chlorides of the following acids: acetic, benzoic, o-toluic, p-toluic, p-nitrobenzoic. The chloromercuri thiophene appears to be a catalyst in these reactions.

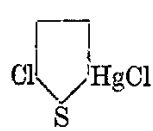
2-Bromomercuri thiophene, obtained from the chloride by action of mercuric bromide, crystallises from toluene in glistening plates, M.pt. 169° to 170° C., somewhat easily soluble in acetone, with difficulty in cold alcohol, chloroform, benzene, or carbon bisulphide.

2-Iodomercuri thiophene may be prepared in a similar manner to the bromide, or by treating an acetone solution of mercury 2 : 2′-dithienyl with one molecule of sodium iodide. It crystallises in shining, silvery plates, melting at 117° C., insoluble in water, not easily in hot alcohol or cold benzene, readily in hot benzene or cold acetone. Since the iodide is affected by sunlight, turning red, all the operations in connection with its extraction should be carried out in absence of sunlight. It reacts with thallic chloride to give thallous chloride and 2-chloromercuri thiophene,[3]

2-Thiocyanatomercuri thiophene is obtained from an acetone solution of 2-chloromercuri thiophene by treatment with 1 mol. of sodium thiocyanate. The mercury-2 : 2′-dithienyl is filtered off and the thiocyanate precipitated from the filtrate by water. It crystallises from toluene in glistening plates, melting at 179° to 180° C. It is easily soluble in acetone, sparingly in cold alcohol, ethyl acetate, benzene, or toluene, insoluble in water.

2 : 5 Dichloromercuri thiophene is obtained as a by-product in the preparation of the monomercurichloride, or by treating the corresponding acetate solution with sodium chloride. It is a white powder, insoluble in all indifferent solvents, not easily attacked by acids, even concentrated nitric acid, and is unaffected by aqueous alkalies. When boiled under reflux with aqueous bromine for one hour it yields a mixture of di-, tri-, and tetrabromothiophenes, but warmed with aqueous iodine only di-iodothiophene is obtained.

5-Chloromercuri-2-chlorothiophene,



is prepared in the usual way from 2-chlorothiophene and mercuric chloride in sodium acetate solution. It forms glistening silver plates, M.pt. 218° to 219° C., and has the usual solubility. Traces of a *di-mercurated* compound are also obtained, melting at 278° to 280° C. with decomposition.

[1] Steinkopf, *Annalen*, 1917, 413, 310.
[2] Steinkopf, *ibid.*: Finzi, *Gazzetta*, 1915, 45, ii. 280.
[3] Goddard, *Trans. Chem. Soc.*, 1923, 123, 1169.

The corresponding *bromide* forms fine white crystals, M.pt. 191° C., from toluene solution, and is obtained by treating an acetone solution of mercury 5 : 5′-dichloro-2 : 2′-dithienyl with mercuric bromide.

The *iodide* is formed from the chloride by treatment with sodium iodide in acetone solution. It crystallises in white, glistening plates which melt at 126° to 126·5° C. with partial decomposition. It is easily soluble in ethyl acetate or acetone, somewhat soluble in alcohol, benzene, chloroform, or carbon bisulphide in the cold, insoluble in water. It tends to split off mercuric iodide when in solution.

5-Chloromercuri-2-bromothiophene yields fine crystals, melting at 225° C. It is not very soluble in cold solvents, with the exception of acetone. The *bromide* forms white, matted needles, M.pt. 197° to 197·5° C., whilst the *iodide* crystallises in small white crystals from alcohol, M.pt. 119° C., easily soluble in carbon bisulphide, acetone, or ethyl acetate, warm benzene, xylene, alcohol, or chloroform. It is sensitive to light, becoming pale red.

5-Chloromercuri-2-iodothiophene yields slender, matted crystals, sintering about 215° C. and melting at 225° C. It is fairly soluble in warm benzene or acetone. When heated with acetyl chloride at 80° to 90° C. it gives 2-iodo-5-acetothienone, and when refluxed with iodine and water for a few minutes until the iodine disappears, 2 : 5-di-iodothiophene is obtained. The *bromide*, on crystallising from xylene, forms matted crystals darkening at 170° C., is somewhat soluble in acetone, difficultly soluble in carbon bisulphide, and practically insoluble in alcohol or benzene. The *iodide* is partially decomposed when recrystallised from xylol, and is a faint yellow, micro-crystalline body, M.pt. 141° to 142° C. It is moderately soluble in acetone, readily soluble in warm chloroform, benzene, or xylene.

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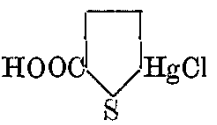
5-Chloromercuri-2-carboxyl-thiophene,



is prepared in the usual manner from thiophene-2-carboxylic acid. It occurs in two forms: (*a*) soluble in sodium hydroxide and reprecipitated by dilute hydrochloric acid as a white, amorphous body, and (*b*) insoluble in sodium hydroxide, but soluble in ammonium hydroxide, and reprecipitated by dilute hydrochloric acid. Both compounds melt at 297° to 298° C., with violent gas evolution.

5-Chloromercuri-2-methyl thiophene.—Cold saturated mercuric chloride (220 grams), 44 grams of 33 per cent. sodium acetate and 2·6 grams of 2-methyl thiophene in 150 c.c. of alcohol give 8·6 grams of product in thirteen hours.[1] It crystallises from alcohol in glistening needles, M.pt. 204° C.[2] It is insoluble in water or ether, and with benzoyl chloride yields phenylthiotolyl ketone.

5-Chloromercuri-2-phenyl thiophene occurs as white, glistening plates, melting at 234° C. and slightly soluble both in alcohol and in benzene.

?-Chloromercuri-3-methyl thiophene is prepared from β-thiotoluene in the usual way. A *mono-* and a *di-mercurated* compound result.

[1] Steinkopf and Bauermeister, *Annalen*, 1914, 403, 59.
[2] Volhard gave 197° C.

the former crystallising from alcohol in white, bushy needles, the di-compound being insoluble in the usual organic solvents, and only attacked with difficulty by concentrated nitric acid.

?-Chloromercuri-3-isopropyl thiophene crystallises from hot alcohol in shining, long, white needles, M.pt. 137° C., soluble in ether, insoluble in water. A *dichloro* compound is formed at the same time as a white granular mass, insoluble in all solvents and very stable towards concentrated nitric acid.

5-Thiocyanatomercuri-2-chlorothiophene,—The corresponding 5-chloromercuri compound (3·5 grams) in 120 c.c. of acetone is treated with 0·8 gram (1 mol.) of sodium thiocyanate in 15 c.c. of acetone. Yield 2·9 grams. It crystallises from benzene or alcohol in glistening silver plates, melting at 187° C. after previously sintering. It is readily soluble in cold acetone, moderately soluble in cold alcohol or ethyl acetate, but readily soluble on warming, sparingly in hot benzene or ether. The thiocyanate may also be obtained from mercury 5 : 5′-dichloro-2 : 2′-dithienyl by the action of mercury thiocyanate in acetone solution. On the other hand, if 2 mols. of sodium thiocyanate are used in the first preparation, mercury 5 : 5′-dichloro-2 : 2′-dithienyl is isolated.[1]

5-Thiocyanatomercuri-2-bromothiophene crystallises from ethyl acetate in small, warty aggregates, M.pt. 187° to 188° C., easily soluble in pyridine, sparingly in cold ethyl acetate or alcohol. If two molecules of sodium thiocyanate be used, mercury 5 : 5′-dibromo-2 : 2′-dithienyl, M.pt. 182° to 183° C., is formed.

5-Thiocyanatomercuri-2-iodothiophene.—It was found impossible to isolate this compound in the pure state using the 5-iodomercuri derivative, so that the preparation was conducted as follows :—Three grams of mercury 5 : 5′-di-iodo-2 : 2′-dithienyl and 1·54 grams of mercury thiocyanate in 250 c.c. of acetone were heated to boiling. The liquid on filtering deposited 1·1 grams of substance, and a further 2·8 grams were thrown out by the addition of water. The product yielded crystals from nitromethane solution, M.pt. 173° C., easily soluble in warm acetone or cold pyridine, sparingly in cold nitromethane or bromobenzene, readily on heating. In alcohol, benzene, or xylene it is only sparingly soluble.

5-Chloromercuri-2-n-propylthiophene.—A mixture of 193 grams of mercuric chloride, 38 grams of sodium acetate, 450 c.c. of alcohol, and 3 grams of n-propylthiophene after six days deposits 6·2 grams of crystals. Yield 72 per cent. The crystals from benzene melt at 155° C., are easily soluble in pyridine, warm alcohols, benzene, or toluene, sparingly in warm ether.

5-Thiocyanatomercuri-2-n-propylthiophene is readily obtained from the above compound in the usual manner. It crystallises from toluene in silvery plates, M.pt. 169° to 169·5° C., easily soluble in cold acetone, fairly soluble in benzene or toluene, sparingly in alcohol.

5-Chloromercuri-2-isoamylthiophene is obtained in 75 per cent. yield after the reaction mixture has stood for four days. It crystallises from benzene in fine needles, M.pt. 171·5° to 172° C., readily soluble in cold acetone or warm ether, sparingly in other cold solvents. If treated with sodium iodide it yields mercury 5 : 5′-di-isoamyl-2 : 2′-dithienyl.

5-Thiocyanatomercuri-2-isoamylthiophene forms glistening crystals, M.pt. 199° to 200° C.

[1] Steinkopf, *Annalen*, 1921, 424, 36.

5-Chloromercuri-2-benzylthiophene is obtained in 80 per cent. yield in four days. It yields small, snow-white crystals from toluene, M.pt. 189° to 191° C., having the usual solubilities. It does not yield a thiocyanato compound, but mercury 5 : 5′-dibenzyl-2 : 2′-dithienyl is formed instead.

5-Thiocyanatomercuri-2-methylthiophene is deposited as pure white, microscopic crystals from ethyl acetate. It decomposes at 202° to 204° C., and when crystallised from xylene it is partially decomposed. It is readily soluble in pyridine or acetone, and the following solvents when heated: alcohols, ethyl acetate, or xylene. When 2 mols. of sodium thiocyanate are used in the preparation a body melting at 203° to 204° C. is isolated.

5-Bromomercuri-2-methylthiophene.—To prepare this substance mercury 5 : 5′-dimethyl-2 : 2′-dithienyl (1·97 grams) and 1·8 grams of mercuric bromide in 100 c.c. of acetone are rapidly brought to the boil, then cooled in ice. The bromide is precipitated by the addition of water. Yield 3·5 grams. It crystallises from ethyl acetate in shining, white needles, melting at 179° to 180° C., and having the usual solubilities.

5-Iodomercuri-2-methylthiophene, prepared in a similar manner to the bromide, crystallises from alcohol in silvery needles melting at 111° to 112° C. It is readily soluble in cold ethyl acetate or benzene, less so in acetone unless heated.

5-Chloromercuri-2-ethylthiophene may be crystallised from alcohol; M.pt. 147° to 148° C. Yield 81 per cent.

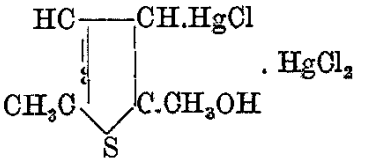
5-Thiocyanatomercuri-2-ethylthiophene yields small plates from benzene; M.pt. 167·5° to 169° C.

5-Iodomercuri-2-ethylthiophene, prepared from the chloride using rather more than 2 mols. of sodium iodide in acetone solution, crystallises from much alcohol in silvery needles melting at 96° to 97° C., affected by light.

(2 or 5)?-Thiocyanatomercuri-3-methylthiophene yields small crystals from benzene, melting at 169° C., sparingly soluble in acetone in the cold, easily when heated, but only sparingly in warm benzene or toluene.

5-Hydroxymercuri-2-acetoxymercuri thiophene occurs as hair-fine needles, M.pt. 270° C. It is obtained from commercial benzene by boiling it with mercuric acetate. One kilogram of benzene, 40 grams of mercuric acetate, 300 c.c. of water, and 40 grams of acetic acid after boiling under reflux for thirty minutes give 32 grams of compound.[1] It is only soluble in acetic acid, from which it crystallises as the *diacetate*; dry distillation with concentrated hydrochloric acid yields thiophene and mercuric chloride.

3-Chloromercuri-2-hydroxy-2 : 3-dihydro-2 : 5-dimethylthiophene mercuric chloride,[2]



This compound is derived from 2 : 5-dimethylthiophene in the usual

[1] Dimroth, *Ber.*, 1899, **32**, 758; Schwalbe, *ibid.*, 1905, 38 ,2208.
[2] Steinkopf, *Annalen*, 1921, **424**, 23.

manner. It forms white crystals, M.pt. 186° to 187° C., insoluble in water, difficultly soluble in ether, cold alcohol, chloroform, or benzene, easily soluble in acetone or warm solvents.

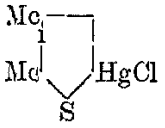
3-Chloromercuri-2 : 5-dimethylthiophene is contained in the mother-liquors from the above compound, and may be precipitated by the addition of water. It crystallises from alcohol in silky needles, M.pt. 156° to 157° C., insoluble in water, easily soluble in acetone or warm alcohol. It is also formed when the preceding mercuric salt is boiled for a long time with a little alcohol. The *thiocyanate* crystallises from benzene in snow-white crystals, M.pt. 177° to 177·5° C.

The corresponding *iodomercuri* compound is obtained by treating the above chloride in acetone solution with sodium iodide. It crystallises from benzene in white, glistening needles, M.pt. 175° C.

2-Chloromercuri-3 : 4-dimethyl thiophene occurs as white needles, M.pt. 137° to 138° C., easily soluble in warm benzene, chloroform, or cold acetone, slightly soluble in water. The crude product obtained in this preparation gives a residue insoluble in boiling alcohol and in the usual organic solvents. It is **2 : 5 - dichloromercuri-3 : 4-dimethyl thiophene**, which does not melt at 270° C.

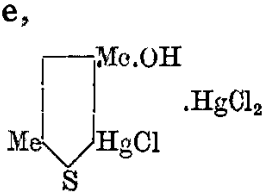
The corresponding 2-*iodomercuri* compound is prepared from acetone solutions of the chloride and sodium iodide. It gives yellowish plates from benzol, M.pt. 142° C., easily soluble in acetone, carbon bisulphide, chloroform, or warm benzene and toluene, sparingly in alcohol. The *thiocyanato* compound, recrystallised from alcohol, melts at 178° to 179° C.

5-Chloromercuri-2 : 3-dimethylthiophene,



may be prepared from 140 grams of mercuric chloride solution, 30 grams of sodium acetate solution, 140 grams of alcohol, and 2 grams of 2 : 3-dimethylthiophene. A yield of 6 grams (97 per cent.) is obtained in five days. It crystallises from benzene in matted crystals, M.pt. 213° to 214° C., easily soluble in cold pyridine or quinoline and sparingly in acetone unless heated. No dichloromercuri compound is obtained. The *thiocyanato* derivative forms matted crystals from much ethyl acetate, decomposing on heating at about 240° C.

5-Chloromercuri-4-hydroxy-4 : 5-dihydro-2 : 4-dimethylthiophene mercuric chloride,

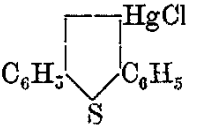


A saturated solution of mercuric chloride (264 grams), 54 grams of 33 per cent. sodium acetate, 240 grams of alcohol, and 3·6 grams of 2 : 4-dimethylthiophene are allowed to stand for fifteen hours, when 12·7 grams of precipitate are collected. Yield 62 per cent. It forms fine crystals from benzene, M.pt. 167° to 168° C., and has the usual solubilities.

5-Chloromercuri-2 : 4-dimethylthiophene.—When 41 grams of the above compound are boiled for thirty minutes with 500 c.c. of alcohol,

19 grams of product are obtained, the filtrate yielding unchanged mercuric chloride addition product. After two crystallisations the body melts at 138° to 139° C. It is readily soluble in cold acetone, moderately soluble in carbon disulphide, sparingly in cold benzene, ethyl acetate, or alcohol, but easily soluble on heating. With sodium thiocyanate (2 mols.) in acetone solution, it yields mercury 2 : 4 : 2′ : 4′-tetramethyl-5 : 5′-dithienyl. The corresponding *thiocyanato* compound is crystallised from alcohol, sinters at 170° C., and melts at 173° to 175° C. It is only sparingly soluble in the usual solvents in the cold and not very readily on heating.

3-Chloromercuri-2 : 5-diphenylthiophene,

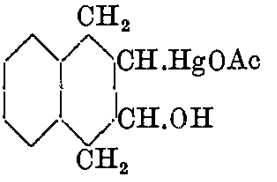


In order to prepare this substance 2 : 5-diphenylthiophene (1·4 grams) in 600 c.c. of alcohol is treated with 50 grams of saturated mercuric chloride solution and 10 grams of 33 per cent. sodium acetate solution, and after twelve days a 0·3 gram or 11 per cent. yield is formed. The reaction can be made quantitative by altering the above quantities to 4 grams of the thiophene in 400 c.c. of alcohol, 160 grams of sublimate solution and 28 grams of acetate solution, and boiling the mixture for two and a half hours. The whole is filtered, washed with a little cold alcohol, and recrystallised from xylene. It forms matted crystals, melting at 221° to 222° C., readily soluble in acetone or in hot xylene or toluene, sparingly in cold benzene, chloroform, or alcohol. It is transformed by sodium thiocyanate (2 mols.) in acetone, to mercury 2 : 5 : 2′ : 5′-tetraphenyl-3 : 3′-dithienyl. The latter substance with mercury thiocyanate in acetone is converted into the 3-*thiocyanatomercuri* derivative, which sinters at 180° to 200° C., but remains black and unmelted at 265° C.

DropBooks

Dihydronaphthalene Compounds.

2-Acetoxymercuri-3-hydroxy-tetrahydronaphthalene,[1]



A mixture of naphthalene and dihydronaphthalene is dissolved in ether and shaken with an aqueous solution of mercuric acetate. After twenty-four hours long needles of the acetate separate. It may be recrystallised from benzene or ligroin, the product melting at 122° C. It is soluble in potassium hydroxide, and if potassium bromide be added and carbon dioxide passed in, the *bromide* is precipitated. It crystallises from benzene in glistening crystals, M.pt. 159° C. The corresponding *iodide* is prepared from the acetate by treatment with potassium iodide, and when crystallised from benzene melts at 156° C., turning red. All the above salts are decomposed by 30 per cent. hydrochloric acid, naphthalene-free dihydronaphthalene being regenerated.

[1] Sand and Gennsler, *Ber.*, 1903, 36, 3699.

Mercury Derivatives of Aromatic Compounds containing Halogen, Nitro, or Sulphonic Acid Groups.

In the case of halogen-substituted hydrocarbons it has been found that the sulphinic acid method of introducing the mercury gives the best results,[1] and it is preferable to methods of direct mercuration using mercuric acetate at high temperatures.

p-Chlorophenylmercuric acetate.—p-Chlorobenzene sulphinic acid, prepared from p-chloroaniline by Gatterman's method, is dissolved in glacial acetic acid, and a solution of three molecular equivalents of mercuric acetate in the same solvent added, and the whole boiled for fifteen minutes. The sulphinic acid is completely converted to the mercury compound, and is obtained by filtering the reaction mixture, and precipitating with water. Yield 70 per cent. The acetate is a white, crystalline solid, M.pt. 193° C., which yields pure p-chloronitrobenzene when treated with concentrated nitric acid at 65° C. for ten minutes. A suspension of the acetate in 10 per cent. aqueous potassium bromide, when treated with a slight excess of 10 per cent. bromine in 10 per cent. potassium bromide and shaken for one hour, yields p-chlorobromobenzene.

p-Chlorophenylmercuric chloride is obtained by treating an alcoholic solution of the acetate with 10 per cent. sodium chloride. It is a white solid, M.pt. 225° C., and may be crystallised from alcohol.

p-Bromophenylmercuric acetate, a white crystalline solid, M.pt. 196° C., is prepared as the chloro compound. It may be converted by nitric acid to p-bromonitrobenzene, and by sodium chloride to the corresponding *chloride*, M.pt. 250° C.

p-Iodophenylmercuric acetate, which melts at 191° C., is also known. The mercury may be replaced by bromine in potassium bromide solution, giving a bromo-iodobenzene.

o-Chlorophenylmercuric acetate is a white, crystalline solid, M.pt. 115° C.; the corresponding *chloride* melts at 145° C.

o-Bromophenylmercuric acetate may be prepared in the usual way. It melts at 124° C.; the *chloride* melts at 155° C. and sublimes at 100° C. It yields o-dibromobenzene when treated with bromine in acetic acid solution.

m-Chlorophenylmercuric acetate is a white solid, melting at 133° C. It is soluble in alcohol, glacial acetic acid, benzene, or acetone, and slightly soluble in ether. The *chloride* is best recrystallised from alcohol and melts at 210° C.

m-Bromophenylmercuric acetate is a white, crystalline solid, melting at 160° C. The *chloride* melts at 190° C. and yields m-dibromobenzene by the usual treatment.

Derivatives of Nitrobenzene.

o-Nitrophenylmercuric chloride, $NO_2.C_6H_4.HgCl$,[2] is prepared as follows:—

1. Mercuric acetate, together with five times its weight of nitro-

[1] Hanke, *J. Amer. Chem. Soc.*, 1923, 45, 1321.

[2] Dimroth, *Ber.*, 1902, 35, 2032; *Annalen*, 1925, 446, 148; Kharasch and Chalkley, *J. Amer. Chem. Soc.* 1921, 43, 607.

benzene, is heated in an oil-bath to 150° C. until a test portion treated with dilute sodium hydroxide does not give a precipitate of mercuric oxide. When the mass is cooled a small quantity (0·6 per cent.) of mercuric acetate crystallises out, and the mixture is filtered, the filtrate being decomposed by sodium chloride, and steam distilled. After cooling, a solid is obtained which is dried and extracted with ligroin, from which solvent pale yellow needles are deposited, several recrystallisations from acetic acid giving small, yellowish plates, M.pt. 181° to 182° C. (Dimroth).[1]

2. The starting material in this preparation is o-nitrobenzene sulphinic acid, which may be prepared from o-nitroaniline by the diazo-reaction. Two grams of this acid in 20 c.c. of alcohol are added to 6 grams of mercuric chloride in a mixture of 20 c.c. of alcohol and 20 c.c. of water, and the resulting solution boiled for forty-five minutes. The precipitate is extracted with acetone, the solvent evaporated, and the residue crystallised from 95 per cent. alcohol, when faint yellow crystals, M.pt. 185° C. (corr.), are obtained. Yield 3 grams (78 per cent.).

The chloride is very soluble in acetone, soluble in hot alcohol or ether, only slightly soluble in water. When treated with bromine in potassium bromide for two hours on a shaking machine, and then extracted with ether, o-bromonitrobenzene, M.pt. 41° to 42° C., is obtained, which shows the mercury to be in the ortho position to the nitro group. No mercuric sulphide is obtained when the chloride is acted upon by ammonium sulphide, but when boiled with hydrochloric acid nitrobenzene results. During the direct mercuration of nitrobenzene, *mercury o-o'-dinitrodiphenyl*, M.pt. 206° C., is also formed.[2]

m-Nitrophenylmercuric chloride.—Eight grams of the sodium salt of m-nitrobenzene sulphinic acid in 40 c.c. of water are added to 21 grams of mercuric chloride in 100 c.c. of alcohol, and slightly more glacial acetic acid added than is required to liberate the sulphinic acid, after which the mixture is boiled for twenty hours. Extraction of the residue with acetone and recrystallisation from alcohol gives white crystals, melting at 236° to 237° C. Yield 5·7 grams (42 per cent.). The compound is less soluble in acetone or alcohol than the ortho derivative.

p-Nitrophenylmercuric chloride is prepared in a similar manner to the ortho compound, but the yields are very poor, even after fifteen hours' boiling. It crystallises from alcohol in colourless crystals, M.pt. 265° to 266° C. (corr.) with decomposition.

2 : 4 : 6-Trinitrophenylmercuric chloride, $C_6H_2(NO_2)_3.HgCl$, melting at 202° C., is obtained by heating 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenyl with alcoholic mercuric chloride. When treated in aqueous suspension with iodine in potassium iodide solution it yields 2 : 4 : 6-trinitro-iodobenzene.[3]

Derivatives of Nitrotoluenes.

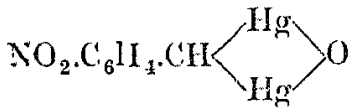
Ortho and p-nitrotoluenes are readily converted to mercury derivatives when boiled with mercuric oxide in the presence of sodium hydroxide, the metal in the compounds entering the side chain under these conditions. The derivatives of p-nitrotoluene and 2 : 4-dinitro-

[1] See Dimroth, *Annalen*, 1926, 446, 148; Jürgens, *Rec. trav. chim.*, 1926, 45, 61.
[2] Wibaut and Jürgens, *Verslag. Akad. Wetensch. Amsterdam*, 1922, 29, 1074.
[3] Kharasch, *J. Amer. Chem. Soc.*, 1921, 43, 2238.

toluene, however, are very difficult to obtain in the pure state, but o-nitrotoluene yields two well-defined compounds.[1]

o-Nitrobenzylmercuric chloride, $NO_2.C_6H_4.CH_2.HgCl$, yields colourless needles, M.pt. 145° to 146° C., easily soluble in acetone or benzene, with difficulty in alcohol or ether; from its solutions in caustic alkali it is precipitated by acid.[2]

o-Nitrodimercuribenzylidene oxide or anhydride of o-nitrobenzal dimercuric hydroxide,



The mercuric oxide obtained from 297 grams of mercuric chloride by treatment with cold sodium hydroxide is well washed and added to a solution of 44 grams of sodium hydroxide in 2500 c.c. of water and the whole heated to boiling under a reflux condenser, bumping being prevented by passing in a current of air. o-Nitrotoluene, 75 grams, is then added in small portions, the operation taking nine hours, and the whole is then boiled for 1·5 hours. From this mixture 291 grams of crude, dry oxide are obtained, yield 96·4 per cent. When hydrochloric acid is added to the mother-liquors 5·2 grams of crude o-nitrobenzylmercuric chloride are precipitated. The crude oxide is dissolved in acetic acid, and precipitated by adding excess of sodium hydroxide, when dark yellow, crystalline masses are isolated, M.pt. 220° C.

The oxide is partially decomposed by hydrogen sulphide into mercuric sulphide and o-nitrotoluene, and by zinc dust and sulphuric acid it is reduced to o-nitrotoluene and mercury. When heated with nitrous acid it gives o-nitrobenzaldehyde, which is also formed together with a small proportion of o-dinitrotolane, $NO_2.C_6H_4.C{\equiv}C.C_6H_4.NO_2$, by boiling with nitric acid. The oxide, when treated in the cold with nitrous and hydrochloric acids, yields approximately molecular proportions of o-nitrobenzaldehyde and its oxime, the dinitrite formed by the nitrous acid being converted into the oxime by the hydrochloric acid, *via* a hypothetical nitroso derivative :

$$NO_2.C_6H_4.CH(HgNO_2)_2+2HCl=HNO_2+H_2O+NO_2.C_6H_4.C(NO)(HgCl)_2$$
$$NO_2.C_6H_4.C(NO)(HgCl)_2+2HCl=NO_2.C_6H_4.CH{=}NOH+2HgCl_2$$
$$2NO_2.C_6H_4.CH{=}NOH+4HNO_2=2NO_2.C_6H_4.CHO+4NO+N_2O+3H_2O$$

The oxide is in general very stable towards acids and alkalies, but when boiled with 20 per cent. hydrochloric acid it is transformed into anthranil. Treatment with chlorine in presence of an excess of hydrochloric acid gives o-nitrobenzylmercuric chloride, and bromine and iodine yield the corresponding halides.

The following salts have been prepared :—

Sulphate, $NO_2.C_6H_4.CH{=}Hg_2{=}SO_4$.—Forms pale yellow, broad needles or plates, giving with sodium hydroxide the free base, and on boiling with water an orange-yellow, basic sulphate, $(NO_2.C_6H_4.CH(HgOH)Hg)_2SO_4$.

Chloride, a pale yellow, amorphous compound, formed by adding dilute

[1] Reissert, *Ber.*, 1907, 40, 4209; German Patents, 182217, 182218; see Burton, Hammond, and Kenner, *J. Chem. Soc.*, 1926, p. 1802.

[2] For preparation, see oxide, below.

hydrochloric acid to the base, and when boiled for 4·5 hours with sodium chloride solution, it is converted into a yellow hydroxychloride, $NO_2.C_6H_4.CH(HgCl).HgOH$.

Nitrate, pale yellow, by triturating the base with dilute nitric acid.

Nitrite, by mixing the base with water, shaking with sodium nitrite, then with 10 per cent. sulphuric acid.

p-Nitrobenzylmercuric chloride has only been obtained in an impure state by the above method, the product being converted into p-nitrobenzoic acid when treated with dilute nitric acid.

2 : 4-Dinitrodimercuribenzylidene oxide.—Dinitrotoluene (18·2 grams) and 54·2 grams of mercuric chloride are dissolved in 600 c.c. of absolute alcohol, and to the solution 13·8 grams of sodium in 270 c.c. of absolute alcohol are quickly added, whilst the solution is rapidly stirred. A brownish-red, voluminous precipitate immediately separates, this being filtered off, washed with alcohol, then boiled several times with water to remove hydrochloric acid. Yield 58 grams. The product thus obtained is difficult to purify. When treated with hydrogen sulphide or 10 per cent. hydrochloric acid it yields 2 : 4-dinitrotoluene, and with the former reagent mercuric sulphide in addition. Concentrated nitric acid converts it to 2 : 4-dinitrobenzoic acid.

Although in the preceding compounds, formed by the interaction of nitrotoluenes and mercuric oxide in hot sodium hydroxide solution, the mercury enters the side chain, it has recently been shown [1] that the mercury enters the nucleus when mercuric acetate and nitrotoluene are heated together at 140° C.

4-Chloromercuri-2-nitrotoluene.—One part of mercuric acetate and 4 parts of o-nitrotoluene are gradually heated with occasional shaking. The melt becomes orange-red at 110° to 120° C. and liquefies to a pale yellow solution as the temperature rises. A temperature of 140° to 150° C. is maintained until a test indicates the absence of mercury ions (after about four hours). After twelve hours a brown solid consisting mainly of mercurous acetate separates, and the clear solution is poured into a large volume of ether and left for twenty-four hours. An amorphous solid is deposited which consists of polymercuri compounds, and contains no monoacetoxymercuri derivatives. The ether is removed, the solution treated with sodium chloride solution, and excess of nitrotoluene removed in steam. The heavy, colourless product obtained is broken up and dried. It is first extracted with ether in a Soxhlet apparatus, to remove any o-nitrotoluene, then recrystallised twice from hot acetone, the chloromercuri compound being deposited in silky needles, melting at 220·5° to 221° C. (corr.). It is sparingly soluble in the usual solvents, except acetone and hot glacial acetic acid. With bromine in chloroform, or iodine it yields 4-bromo- or 4-iodo-2-nitrotoluene respectively.

The 4-*bromomercuri* compound is a crystalline powder, M.pt. 241° C., and the *iodide* melts with slight decomposition at 286° C.

The existence of **6-chloromercuri-2-nitrotoluene** has also been proved.

5-Chloromercuri-2-nitrotoluene.—2-Nitrotoluene-5-sulphinic acid is boiled with 50 per cent. aqueous alcoholic mercuric chloride for a week, any precipitate being periodically removed. The latter is washed, dried, and extracted with hot acetone, from which the compound

[1] Coffey, *J. Chem. Soc.*, 1926, p. 637.

separates in small, felted, shining needles, M.pt. 210° C. Its solubilities and general properties are similar to those of the 4-isomeride.

5-Chloromercuri-3-nitrotoluene.[1]—The mercuration is carried out by the method described under 4-chloromercuri-2-nitrotoluene. The crude product of mercuration is extracted with hot acetone, the 5-chloro compound remaining undissolved. It crystallises from glacial acetic acid in colourless, feathery needles, M.pt. 294° C., which yield 5-bromo-3-nitrotoluene by treatment with bromine in potassium bromide solution.

4-Chloromercuri-3-nitrotoluene crystallises from the hot acetone extractions described above. It forms pale yellow needles, sintering at 207° C. and melting at 210° C. (corr.). It may be converted into 4-bromo-3-nitrotoluene. The presence of **6-chloromercuri-3-nitrotoluene** in the mercuration products has also been proved.

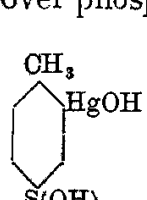
Pure products cannot be obtained by the mercuration of p-nitrotoluene with mercuric acetate at 140° C., so that the derivatives have been prepared from nitrotoluene sulphinic acids.

2-Chloromercuri-4-nitrotoluene is obtained by boiling 4-nitrotoluene-2-sulphinic acid with a 50 per cent. aqueous alcoholic solution of mercuric chloride. The product is washed with 50 per cent. alcohol, dried, and extracted with acetone, the compound separating out in feathery needles, M.pt. 230° to 231° C. (corr.).

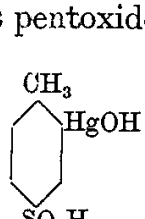
3-Chloromercuri-4-nitrotoluene is prepared from the sulphinic acid in the usual way. It crystallises in colourless needles, M.pt. 226° to 227° C. (corr.), which may be converted into 3-bromo-4-nitrotoluene.

Derivatives of Aromatic Sulphonic Acids.[2]

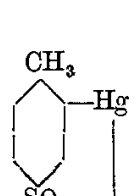
Mercuration of p-toluene sulphonic acid.—The sulphonic acid (190 grams) is dissolved in 750 c.c. of water and 35 c.c. of acetic acid, and the solution boiled and filtered. Mercuric acetate (320 grams) is treated in exactly the same way and the two solutions mixed whilst boiling and boiled for one hour. A sample diluted with an equal volume of water and treated with sodium hydroxide then gives a clear solution, and the mercuration is considered complete. The mixture is filtered whilst boiling, and the solid, 81 grams, rejected; the filtrate on cooling yields 135 grams of a crystalline product. This is extracted with water in a Soxhlet apparatus, a crystalline solid being isolated, which is soluble in warm water, alkali, and salt solutions. When air-dried the formula corresponds to I.; when dried over calcium chloride, II.; and dried *in vacuo* over phosphorus pentoxide, III.



I.



II.



III.

The mercury in these compounds may be replaced by iodine, when 2-iodotoluene-4-sulphonic acid is obtained.

[1] Coffey, *J. Chem. Soc.*, 1926, p. 3215.
[2] Whitmore and Ehrenfeld, *J. Amer. Chem. Soc.*, 1926, 49, 789.

The following substances have also been mercurated, but analysis indicates that the products are mixtures: benzene sulphonic acid and its sodium salt, sodium p-bromobenzene sulphonate, p-iodobenzene sulphonic acid, 2 : 5-dichlorobenzene sulphonic acid, m-nitrobenzene sulphonic acid, o-toluene sulphonic acid and its sodium salt, sodium p-toluene sulphonate, 2-chlorotoluene-5-sulphonic acid. The mercuration of the sodium salts is a much slower process than in the case of the free acids.

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CHAPTER VII.

MERCURY (*continued*).

Derivatives of Aromatic Amines.

All the amines dealt with in the present chapter may be directly mercurated by means of mercuric acetate, but it is impossible to predict how many mercury residues can be introduced into a given compound by comparing it with similar derivatives. This is clearly shown by comparing the chloro- and nitro-anilines. Whilst four different acetoxymercuri derivatives may be obtained from the ortho compound of the former, the meta compound only yields a triacetoxymercuri derivative and the para compound a monomercurated product. o-Nitroaniline, however, gives a monomercurated compound, and the meta and para bodies yield mono- and di-mercurated products.

From the table on p. 112 it will be seen that when a ring-substituted aniline has the para position to the amino group unoccupied, mercury invariably enters that position. A similar statement holds for the ortho position to the amino group, but should these two be filled, the mercury may enter the 6 position, if vacant.

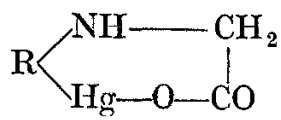
It is also interesting to note that when the amino group in aniline is substituted by basic groups, mercury compounds have always been obtained having the metal in the para position to the amino group, but in the case of the esters of the α-anilido fatty acids, the mercury always enters the ortho position to the substituted amino group, and in some cases the para position as well.

In the case of the naphthylamines, the α-compound yields a diacetoxymercuri derivative, but β-naphthylamine gives only a monomercurated product.

The acetoxymercuri compounds formed above are converted to chloromercuri salts by the addition of sodium chloride, and to the hydroxides by means of sodium hydroxide. When the amino group is not substituted, water may be eliminated between this group and the hydroxymercuri residue, yielding an anhydride, *e.g.* p-aminophenylmercuric hydroxide is considered to exist as

$$\underset{\text{———}}{\text{HN}}.C_6H_4.Hg \quad \text{or} \quad NH{=}C_6H_4{=}Hg$$

In the case of the esters of α-anilido fatty acids and tolylglycine esters, the acetoxymercuri compounds when saponified by sodium hydroxide, eliminate water between the hydroxymercuri residue and the carboxyl group, thus forming anhydrides of the type



The acetoxymercuri derivatives from aniline, substituted aniline, and toluidine compounds, when treated with aqueous sodium thiosulphate give mercuri-bis products of the type R_2Hg, sometimes with the formation of a thiosulphate as an intermediate product,

$$RHg.S_2O_3Na$$

Other modes of forming the mercuri-bis compounds in special cases are as follows :—

1. 6-Acetoxymercuri-2 : 4-dichloroaniline with sodium hydrogen sulphate gives 6-mercuri-bis-2 : 4-dichloroaniline.

2. p-Mercuri-bis-monomethylaniline is formed from the corresponding hydroxide by the action of sodium sulphide.

3. p-Mercuri-bis-dimethylaniline may be obtained by the preceding method, or from p-bromodimethylaniline by the action of sodium amalgam in the presence of ethyl acetate, or from the chloromercuri derivative by the action of metallic copper in pyridine solution.

4. o-Acetoxymercuri-p-bromodimethylaniline is converted into the R_2Hg compound by boiling for eight hours with potassium iodide in alcoholic solution.

5. Mono- and diethylaniline derivatives undergo the same reactions as under 2 and 3.

The diacetoxymercuri-o-chloroanilines when treated with sodium thiosulphate give compounds containing two benzene nuclei attached by two mercury bridges, and a doubly bridged mercury compound is also obtained when 2 : 2′ : 4 : 4′-tetrachloromercuri diphenylamine is boiled with pyridine.

The following derivatives are stable towards ammonium sulphide : p-acetoxymercuri-o-nitroaniline, o-acetoxymercuri-p-bromodimethylaniline, 2 : 4-diacetoxymercuri-α-naphthylamine, and p-dimethylaminophenylmercuric acetate. If the latter compound be boiled with potassium iodide solution, then treated with hydrogen sulphide, only traces of mercuric sulphide are produced. Mercury compounds from β-naphthylamine, β-naphthylamine-6-sulphonic acid, 1 : 5-naphthylamine sulphonic acid are decomposed by ammonium sulphide, whilst naphthionic acid derivatives are only slowly attacked.

The following methods have been used for substituting mercury residues in amines by halogens, in order to find the position of the mercury in the nucleus :—

1. Treating an acetic acid solution of the compound with chlorine in the presence of calcium chloride.

2. By the action of bromine in acetic acid solution.

3. By the use of iodine in potassium iodide.

4. By treating the compound with potassium perbromide.

The following scheme shows the position taken up by mercury in mercurated amines, the figures on the right indicating the position in the nucleus. The terms mono, di, or tri indicate that a monomercuri, etc., derivative is formed, but its position has not been determined. All the rings are numbered in a clockwise direction commencing from the top, irrespective of the group occupying that position. This method of numbering applies only to the table, the nomenclature in the text being that in current use.

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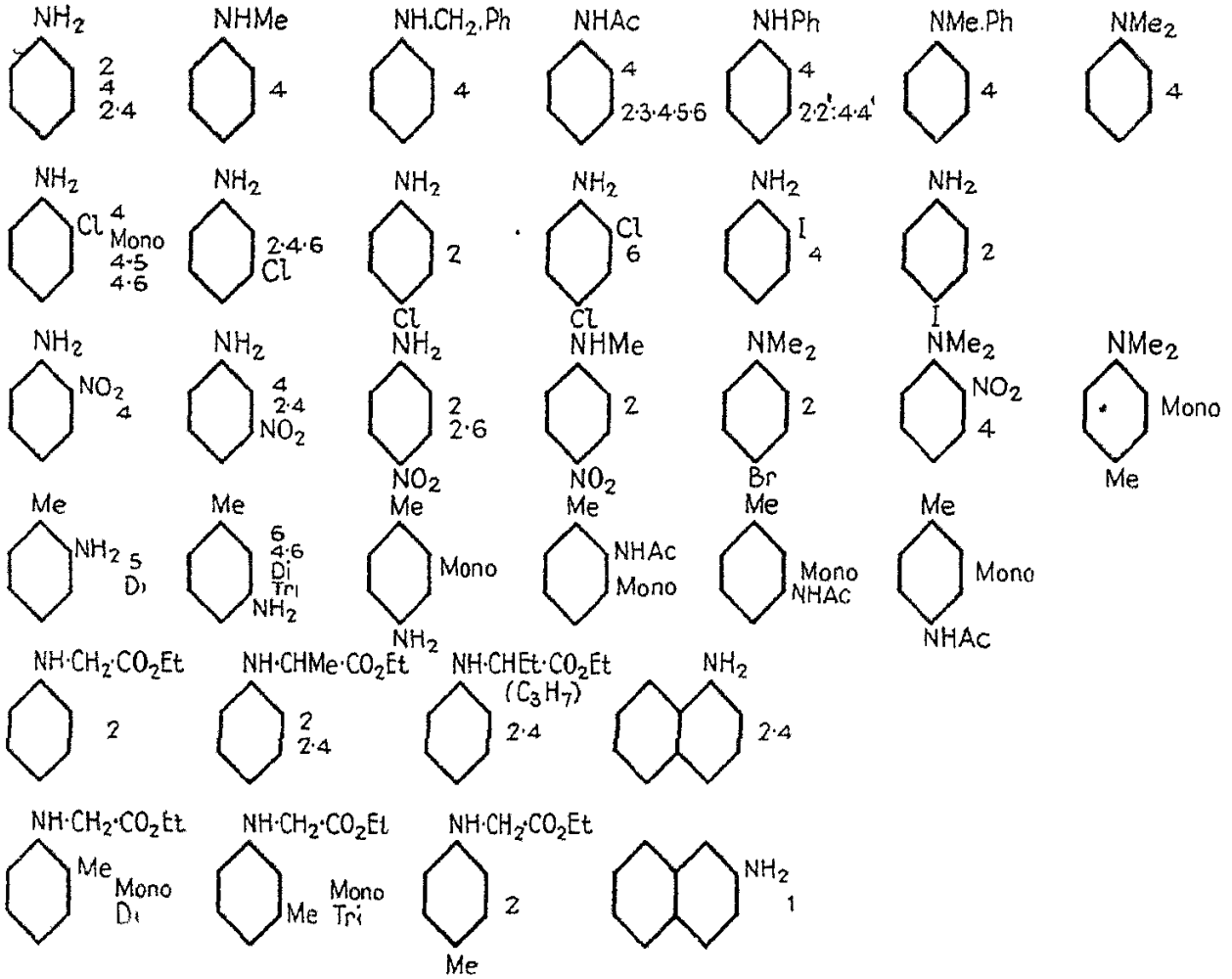
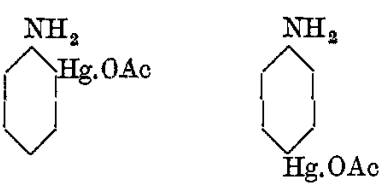


Derivatives of Aniline.

When aniline is treated with mercuric acetate in aqueous solution at room temperature a mixture of o- and p-aminophenylmercuric acetates is formed.



In the earlier work on the mercuration of aniline, the para compound was obtained by Pesci, and he apparently found its molecular weight to be twice that required by the above formula. This error led him to formulate many substituted amines incorrectly, and many of the earlier formulæ have since had to be revised.

p-Aminophenylmercuric acetate.[1]—The most satisfactory method of preparation for this compound is the one described by Dimroth as follows: To 31·8 grams of mercuric acetate in 160 c.c. of water, 18·6 grams of aniline are added. In about three hours, short, thick,

[1] Pesci, *Gazzetta*, 1892, **22**, i. 373; *Atti. R. Accad. Lincei*, 1892, (5), i. 312; *Chem. Zentr.*, 1892, ii. 213; Piccinini and Ruspaggiari, *Gazzetta*, 1892, **22**, ii. 604; Pesci, *Zeitsch. anorg. Chem.*, 1897, **15**, 208; *Gazzetta*, 1897, **27**, i. 567; Dimroth, *Ber.*, 1902, **35**, 2032; Vecchiotti, *Gazzetta*, 1914, **44**, ii. 1350; Reitzenstein and Bönitsch, *J. prakt. Chem.*, 1912, [2], 86, 73.

hard, pale yellow prisms separate. These consist of practically pure p-aminophenylmercuric acetate, and are filtered off. On further standing a second crop of crystals is obtained, but these contain some ortho compound. Yield, 40 grams of pure para and 3 grams of ortho derivative.

Less satisfactory preparations are: (1) Mercuration of aniline acetate with mercuric oxide, (2) from N-mercuri-aniline,

$$C_6H_5NH—Hg—NHC_6H_5$$

by the action of mercuric acetate, acetic acid, or concentrated aniline acetate solutions.

The compound crystallises in prisms, M.pt. 166° to 167° C., is insoluble in water or ether, and with difficulty in alcohol or chloroform, although it may be recrystallised from the latter solvent without change of melting-point. It possesses basic properties, turning red methyl orange yellow in aqueous solution, and it is soluble in dilute mineral and acetic acids. When treated with cold acetic anhydride it yields an *acetyl* derivative, which crystallises as glistening needles from boiling water, M.pt. 220° to 221° C. The same compound was isolated by Pesci from acetanilide and mercuric acetate, the melting-point being given as 218° to 220° C.[1]

Salicylaldehyde in absolute alcohol gives a mercurated Schiff's base, small, yellow crystals decomposing at 185° C.[2]

The acetate can also be diazotised and coupled in the usual way, azo dyes containing mercury being produced.

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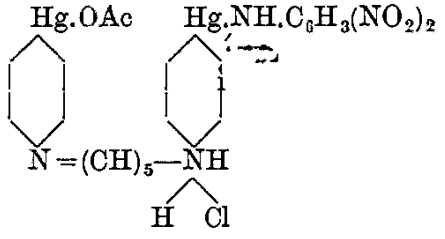
Condensation with Dinitrophenylpyridinium Chloride.[3]

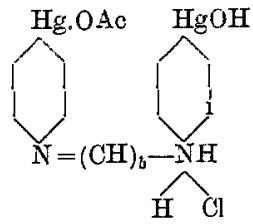
Five grams of the acetate in 450 c.c. of boiling alcohol are treated with 1·2 grams of the pyridine compound in the same solvent. A red coloration immediately appears, and a brown solid separates. The reaction is completed by warming for one hour on the water-bath. The cooled mixture is filtered, the residue washed with alcohol, then extracted with acetone, until no residue remains on evaporation. The dried product is a brown powder, M.pt. 244° C., insoluble in the usual solvents. Yield 3 grams. The substance probably has the following constitution:—



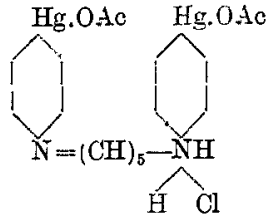
A secondary reaction also takes place, giving a small quantity of substance blackening at 180° C. and not melting at 250° C. This is isolated from the filtrate and corresponds to the formula:

---

[1] Pesci, *Gazzetta*, 1894, 24, ii. 449; 1899, 29, i. 397.
[2] Jacobs and Heidelberger, *J. Biol. Chem.*, 1915, 20, 518.
[3] Reitzenstein and Stamm, *J. prakt. Chem.*, 1910, [2], 81, 154.



If the above reaction be carried out in cold acetone solution, and water added after the reaction is complete, a brown precipitate is thrown down. This is extracted with acetone as before, a brown crystalline powder being obtained. It melts at 164° C., and is insoluble in all solvents. Yield 30 to 40 per cent. The filtrate yields dinitroaniline. The product is formulated as:



Condensation with Propargyl Acetal (acetal of β-ethoxy-acraldehyde).[1]

1. In alcohol—hydrochloric acid solution. Five grams of acetate (2 mols.) in 450 c.c. of alcohol are treated with 0·91 gram of propargyl acetal (1 mol.) and the mixture boiled for six hours. To the cold solution 1·47 grams of 35·39 per cent. hydrochloric acid are added, a pale yellow powder being obtained. It decomposes at 180° C. and no formula has been assigned to it.

2. In aqueous acetic acid solution. The above quantities were again used and the mixture warmed on the water-bath for a day. A yellow body is obtained, 0·3 gram, decomposing at 180° C. This substance agrees with the formula,

$$AcO.Hg.C_6H_4.NH.CH_3{=}N.C_6H_4.Hg.OAc.HOAc$$

When treated with alkali halides, the corresponding p-aminophenylmercuric halides are formed, and with alkali hydroxides the hydroxide is produced.

p-Aminophenylmercuric hydroxide, $NH_2.C_6H_4.HgOH$.—Since it appears doubtful whether this compound exists, it is usually formulated as an anhydride,

$$\underline{HN.C_6H_4.Hg} \quad \text{or} \quad HN{=}C_6H_4{=}Hg$$

The corresponding acetate in dilute caustic alkali is treated with 30 per cent. potassium hydroxide until a precipitate is obtained. This is filtered and dried. Its solutions are strongly alkaline, and it readily forms salts with acids. In water it is only slightly soluble, and if the solution is heated with alkali sulphides a precipitate is formed, which consists of mercuric sulphide and p-mercuri-bis-aniline. The end product of the action of methyl iodide in methyl alcohol solution on the anhydride is $HgI.C_6H_4.NMe_3I$, and when this is treated with barium hydrosulphide, mercuric sulphide is split off and the following substance remains, $Hg(C_6H_4.NMe_3I)_2$).

[1] Reitzenstein and Bönitsch, *J. prakt. Chem.*, 1912, [2], 86, 73.

p-Aminophenylmercuric Halides and Salts.

Chloride.—Five grams of finely powdered acetate are dissolved in 1·5 litres of water, 10 c.c. of saturated sodium chloride solution are added, and the mixture boiled. The solution soon becomes clear, and after filtering glistening plates appear as the solution cools. These when recrystallised from alcohol or benzene melt with decomposition about 188° C.

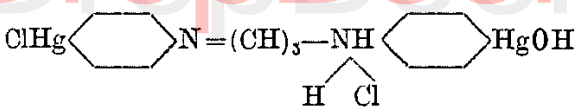
A second form of the chloride is known, this being amorphous. The acetate is dissolved in acetic acid and the calculated amount of aqueous sodium chloride added. The chloride comes down as a faint yellow precipitate. It is insoluble in water, alcohol, or dilute acids.

The crystalline chloride was obtained in 30 per cent. yield by Reitzenstein and Stamm, the acetate and sodium chloride solution being boiled for thirty minutes. The plates, which were recrystallised from benzene, melted at 240° C. When treated with sodium thiosulphate, p-aminophenylmercuric thiosulphate is formed, and from the amorphous form Pesci isolated a crystalline product by the action of alcoholic aniline hydrochloride. It crystallised in fine, colourless needles, decomposing above 150° C.

Condensation with Dinitrophenylpyridinium Chloride.

To 3 grams of the chloride in 500 c.c. of boiling alcohol, 1·29 grams of the pyridine compound in alcohol are added; the solution immediately becomes yellow, and later red. The mixture is boiled for one hour, cooled, and filtered. The reddish-brown residue is washed with boiling acetone, and dried over sulphuric acid. The red-brown powder melts at 125° C., and is insoluble in most organic solvents. Yield 50 per cent. Formula :

DropBooks



If the reaction be carried out in cold acetone, and the pyridine compound dissolved in methyl alcohol, the solution becomes deep red on mixing, and in two hours a reddish precipitate separates. This product melts at 151° C., and is insoluble in most organic solvents. Yield 30 to 40 per cent.

Condensation with Propargyl Acetal.

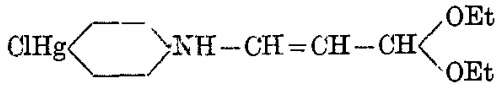
1. In benzene solution. Two grams of the chloride (2 mols.) in 500 c.c. of boiling benzene, and propargyl acetal (1 mol.) are boiled for two hours. Benzene saturated with hydrogen chloride is added, and yellow flocks separate. These are filtered and washed with ether, giving a very light, pale yellow powder.

2. In hydrochloric acid. Five grams of chloride in 200 c.c. of water, 0·78 gram of hydrochloric acid (density 1·19), 0·98 gram of propargyl acetal are warmed for a day on the water-bath. An orange-yellow body (5 grams) separates. It sinters at 210° C. and probably has the formula :

$$HgCl.C_6H_4.N=CH_3.NH.C_6H_4.HgCl$$

Condensation with Ethoxyacrolein Acetal.

If the reaction be carried out as above, an orange-coloured body is obtained, which darkens at 160° C. and melts at 190° C. Formula :



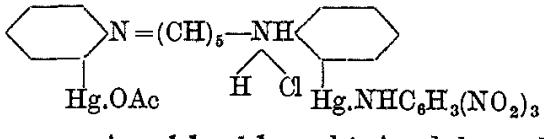
The following p-aminophenylmercuric salts are obtained by the action of the corresponding alkali salts on the acetate : *bromide*, colourless laminæ, M.pt. 182° C. : *iodide*. M.pt. 165° C. (with decomposition) ; *nitrate*, microscopic crystals : *sulphate*, needles, M.pt. 150° C. (with decomposition) ; *thiosulphate*, colourless plates, M.pt. 95° C. (with decomposition).

p-Mercuri-bis-aniline, $(NH_2C_6H_4)_2Hg$.—This product is most readily formed by heating the above thiosulphate with water. p-Mercuri-bis-acetanilide heated at 100° C. in sealed tubes with alcoholic potassium hydroxide yields the same compound. It crystallises in colourless needles, M.pt. 174° C. (with decomposition).

o-Aminophenylmercuric acetate occurs as previously stated in small yield in the mother-liquors from the para compound. It has similar properties to its isomer, and is readily soluble in dilute mineral acids, acetic acid, or dilute alcohol, crystallising from the latter in pearly plates, M.pt. 158° to 160° C. The *acetyl* derivative is made from its components with ice cooling, and crystallises from acetic acid in plates. M.pt. 156° to 158° C. These when treated with aqueous bromine in potassium bromide solution yield o-bromoacetanilide, which proves the constitution of the mercury compound.

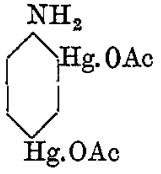
Condensation with Dinitrophenylpyridinium Chloride.

The acetate (2·5 grams) in 400 c.c. of acetone is treated with an acetone solution of the pyridine compound. A slight evolution of heat takes place, the liquid becomes red, and a red precipitate separates. The solvent is evaporated *in vacuo*. Yield 0·7 gram. Formula :



p-Aminophenylmercuric chloride, obtained by adding sodium chloride to the acetate in acetic acid, recrystallises from the latter in long, colourless plates. It may be isolated from the mixed acetates formed during the mercuration of aniline by dissolving them in acetic acid and adding sodium chloride, a mixture of amorphous para chloride and crystalline ortho chloride being obtained. These can be separated by warm alcohol, in which only the ortho chloride is soluble.

2 : 4-Diacetoxymercuri aniline,[1]



[1] Vecchiotti, *Gazzetta*, 1914, 44, ii. 1350 ; *Chem. Zentr.*, 1914, ii. 1350 ; Pesci, *Chem. Zeit.*, 1899, 23, 58 ; *Gazzetta*, 1899, 29, i. 394.

A mixture of 23·25 grams of aniline and 160 grams of mercuric acetate in 200 c.c. of water is allowed to stand for two days. The deposit of crystals is suspended in ammonium acetate solution, brought into solution by the addition of ammonium hydroxide, the mixture neutralised by acetic acid, and the precipitate allowed to stand for twelve hours. It is then washed with dilute acetic acid, and the above operation again repeated. It crystallises in warty prisms, M.pt. 206° C., soluble in acetic acid or ammonium hydroxide, slightly soluble in boiling water, and insoluble in alcohol. When boiled for twelve hours with acetic anhydride, the *acetyl* derivative is formed as colourless, microscopic tetrahedra, M.pt. 220° C. The mercury may be removed by bromine in acetic acid solution, 2 : 4-dibromoacetanilide being obtained, this proving the position of the mercury in the nucleus. When the diacetate is triturated with water and treated with potassium hydroxide, the *dihydroxymercuri* compound is formed. It crystallises in microscopic needles, decomposing at 350° C., slightly soluble in boiling water, insoluble in alcohol.

Derivatives of Halogenated Anilines.

p-Acetoxymercuri-o-chloroaniline.[1]—This product is one of a series of four derivatives obtained from the interaction of o-chloroaniline and mercuric acetate, in aqueous or dilute alcoholic solution. It crystallises from alcohol in white needles, M.pt. 134° C., and when treated with alkali, forms an *hydroxide*, decomposing at 205° C. The latter compound, or the acetate, when treated with aqueous sodium chloride yields the *chloride*, a compound decomposing at 174° C.

The *acetate* when acetylated gives a crystalline product, M.pt. 238° to 239° C., and this when dissolved in acetic acid and treated with calcium chloride and chlorine gives o-p-dichloroacetanilide, showing the position of the mercury in the nucleus.

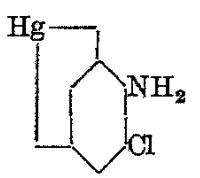
p-Mercuri-bis-o-chloroaniline, M.pt. 138° C., is prepared in the usual manner by the action of sodium thiosulphate on the acetate.

A *second monoacetoxymercuri* compound, isomeric with the above, is isolated from the products of mercuration. It crystallises in yellow needles, M.pt. 143° C., but the position of the mercury has not been determined.

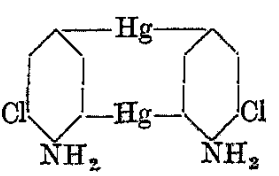
The other two compounds from o-chloroaniline are diacetoxy derivatives.

4 : 6-Diacetoxymercuri-o-chloroaniline, $NH_2.C_6H_2Cl(Hg.OAc)_2$, decomposes at 220° C., and yields an *hydroxide* decomposing at 250° C. and a *chloride* at 190° C. The acetate gives an *acetyl* derivative, M.pt. 230° C., from which 2 : 4 : 6-trichloroaniline may be obtained in the usual way. The *acetyl* derivative of the chloride decomposes at 276° C. The action of sodium thiosulphate on the acetate results in the production of a compound decomposing at 200° C., which is either **4 : 6-mercuri-chloro-aniline** (I.) or **4 : 6-dimercuri-bis-o-chloroaniline** (II.)

(I.)



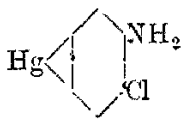
(II.)

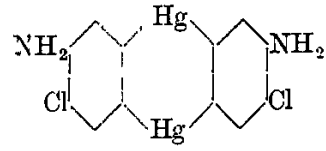


4 : 5-Diacetoxymercuri-o-chloroaniline melts at 232° C., and

[1] Vecchiotti and Michetti, *Gazzetta*, 1925, 55, 372.

its *acetyl* derivative at 230° C. The latter in the usual manner yields 2 : 4 : 5-trichloroacetanilide. Concentrated sodium thiosulphate on the diacetate produces either **4 : 5-mercuri-o-chloroaniline** (III.) or **4 : 5-dimercuri-bis-o-chloroaniline** (IV.), decomposing at 160° C.

(III.) 

(IV.) 

6-Acetoxymercuri-2 : 4-dichloroaniline [1] is prepared in the usual manner from 2 : 4-dichloroaniline and mercuric acetate in dilute alcoholic solution. It melts at 170° to 171° C., forms a *hydroxide* and *chloride*, M.pt. 230° C. and 193° C. respectively. The *acetyl* derivative, M.pt. 283° C., yields 2 : 4 : 6-trichloroacetanilide. In this case a mercuri-bis compound is obtained by the action of sodium hydrogen sulphate on the acetate. It is *6-mercuri-bis-2 : 4-dichloroaniline*, M.pt. 168° C.

When m-chloroaniline is mercurated in aqueous solution, using mercuric acetate, no mono- or diacetoxy derivatives are obtained, but only a triacetoxy compound.[2]

2 : 4 : 6-Triacetoxymercuri-m-chloroaniline melts at 210° C.; the *trihydroxymercuri* and *trichloromercuri* compounds decomposing at 225° C. and 205° C. respectively. The triacetate when acted upon by chlorine in the presence of calcium chloride yields 2 : 3 : 4 : 6-tetrachloroaniline.

o-Acetoxymercuri-p-chloroaniline [3] crystallises in prismatic needles, M.pt. 207° C. It forms a *hydroxide* and *chloride*, the former a white precipitate, and the latter needles, M.pt. 205° C. When acetylated the acetate yields *2-acetoxymercuri-p-chloroacetanilide*, which is converted by chlorine to 2 : 4-dichloroacetanilide.

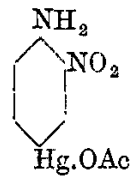
o-Iodoaniline, unlike the corresponding o-chloroaniline, only yields one derivative when treated with mercuric acetate.

4-Acetoxymercuri-o-iodoaniline melts at 149° C.; the *hydroxide* has M.pt. 152° C.; the *iodide*, M.pt. 183° C. With iodine the acetyl derivative gives 2 : 4-di-iodoacetanilide.[4]

Similarly, p-iodoaniline yields **2-acetoxymercuri-p-iodoaniline**, M.pt. 179° C.; an *hydroxide*, M.pt. 259° C.; an *iodide*, decomposing at 165° C.; an *acetyl* derivative, M.pt. 205° C., converted by iodine to 2 : 4-di-iodoacetanilide.

Derivatives of Nitroanilines.[5]

p-Acetoxymercuri-o-nitroaniline,

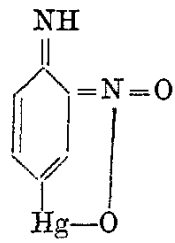


[1] Vecchiotti and Carani. *Gazzetta*, 1926, 56, 147.
[2] Vecchiotti, *Gazzetta*, 1926, 56, 216.
[3] Vecchiotti, *Gazzetta*, 1924, 54, 411.
[4] Vecchiotti and Michetti, *Gazzetta*, 1926, 56, 480.
[5] Kharasch, Lommen, and Jacobsohn, *J. Amer. Chem. Soc.*, 1922, 44, 793.

To a solution of 9·2 grams of mercuric acetate in 15 c.c. of water containing a few drops of acetic acid, a solution of 4·7 grams of o-nitroaniline in 60 c.c. of alcohol is added, and the mixture boiled for one hour. The liquid is filtered whilst hot, and on cooling the compound separates. It is recrystallised from alcohol containing a little acetic acid, yellow crystals being deposited. It does not melt at 300° C., but turns red very gradually. It is stable towards ammonium sulphide.

p-Chloromercuri-o-nitroaniline is obtained from the preceding compound by adding aqueous sodium chloride or alcoholic calcium chloride to its alcoholic solution. It is orange in colour and has no melting-point. Dilute alkali turns it red.

Quinone-(1)-imide aci-(2)-nitro-(4)-mercury,



This compound is produced when any of the mercury derivatives of o-nitraniline are heated in the dry state or treated with dilute sodium hydroxide or even upon boiling with alcohol. The yields are quantitative.

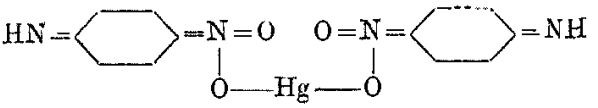
p-Acetoxymercuri-diacetyl-o-nitroaniline, $AcO.Hg.C_6H_3.NO_2.NAc_2$.—The acetate is heated under reflux with acetic anhydride and ethyl acetate. A straw-yellow substance is deposited on cooling, M.pt. 194° C. with decomposition, giving a yellow solution in sodium hydroxide. This compound may be converted to the *monoacetyl derivative* by suspending it in water and adding dilute sodium hydroxide. A yellow solution is formed, from which dilute acetic acid gives a yellow crystalline product. It dissolves in sodium hydroxide, giving a yellow solution which slowly deposits a red precipitate. It decomposes at 194° C. The position of the mercury is proved by shaking the acetyl compound with potassium perbromide, when the mercury is replaced by bromine.

p-Acetoxymercuri-m-nitroaniline.—A solution of 9·6 grams of mercuric acetate in 40 c.c. of water is added to a solution of 4·2 grams of m-nitroaniline in 60 c.c. of alcohol, and the whole heated for three hours on the water-bath. The hot solution is filtered, and the solid residue repeatedly extracted with alcohol containing a little acetic acid. A dark-red residue remains, M.pt. 225° C., which is the diacetoxy compound below. The alcoholic extract is evaporated and the residue recrystallised from a mixture of alcohol and acetic acid. Yellow product, M.pt. 183° C.

o-p-Diacetoxymercuri-m-nitroaniline.—Obtained as above or by boiling an alcoholic solution of 4·2 grams of m-nitroaniline with 19·4 grams of mercuric acetate in aqueous solution until a test gives no mercuric sulphide when reaction mixture is treated with ammonium sulphide. Red compound, M.pt. 225° C. The *acetyl derivative* is a white compound, melting with decomposition at 230° C. The position of the mercury is determined by the aid of potassium perbromide.

o-Acetoxymercuri-p-nitroaniline.—This substance is best prepared similarly to the corresponding o-nitroaniline, but it may also

be isolated by treating the compound shown below with mercuric acetate.



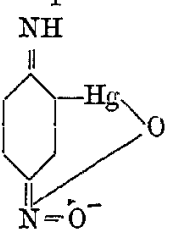
(p-Quinone-imide aci-nitro mercury).

The acetate is a yellow, crystalline compound, which is unchanged at 300° C. Its *acetyl derivative* is a white, crystalline product.

o-Chloromercuri-p-nitroaniline is an orange-yellow product soluble in alkali. It does not melt below 300° C.

2 : 6-Diacetoxymercuri-p-nitroaniline.—An alcoholic solution of 9 grams of p-nitroaniline is boiled with an aqueous solution of 18·4 grams of mercuric acetate. Any monomercuri compound is removed from the residue by washing with hot alcohol containing a little acetic acid, and the product is then dissolved in pyridine to remove any metallic mercury. The addition of acetone precipitates the compound, which is dried *in vacuo*. It is orange in colour and does not melt at 300° C.

Quinone-(1)-imide aci-(4)-nitro-(2)-mercury is formed by treating any of the preceding compounds with dilute alkali, heating alone



or with alcohol. The compound is maroon in colour, and with acetic or hydrochloric acid gives the *acetate* or *chloride* respectively, which do not melt below 300° C.

o-Mercuri-bis-p-nitroaniline, $(C_6H_3.NH_2.NO_2)_2Hg$.—The acetate is moistened with alcohol, suspended in water, and aqueous sodium thiosulphate added. Solution takes place, and the whole is boiled for six minutes; a yellow precipitate soon forms. It is purified by extraction with alcohol. Yield 86 per cent.

Derivatives of Mono- and Di-alkylanilines.

p-Methylaminophenylmercuric acetate, $NHMe.C_6H_4.Hg.OAc$.[1]—The preparation is carried out in the usual manner from mercuric acetate and monomethylaniline in aqueous alcoholic solution. The compound crystallises in glistening plates, M.pt. 149° C. with decomposition; it is soluble in hot alcohol or dilute acetic acid, insoluble in ether or water. When treated with potassium hydroxide, the *hydroxide* is formed. This crystallises in pearly plates, containing water of crystallisation, and melts at 118° C., decomposing at 120° C. It forms strongly alkaline solutions, which have a caustic taste. In alcohol it is readily soluble, sparingly soluble in water, insoluble in ether.

The following salts are also known: *chloride*, yellow, amorphous powder, M.pt. 108° C. with decomposition, becoming green on exposure to light; *bromide*, M.pt. 120° C., has same properties as the chloride;

[1] Pesci, *Gazzetta*, 1893, 23, ii. 521, 529; *Chem. Zentr.*, 1894, i. 501; *Zeitsch. anorg. Chem.*, 1897, 15, 216.

nitrate, hexagonal plates, decomposing suddenly at 150° C.; *sulphate*, microscopic prisms, M.pt. 130° C. with decomposition, becoming grey-green on exposure to light.

p-Mercuri-bis-monomethylaniline is prepared from the hydroxide by the action of sodium sulphide. It crystallises from benzene in lustrous, colourless needles, M.pt. 178° to 179° C., sparingly soluble in alcohol, insoluble in ether.

p-Nitro-o-acetoxymercuri-monomethylaniline.[1] — The following general method of preparation for compounds of this type has been given. One molecule of the compound in a small volume of alcohol is boiled with an aqueous solution containing 0·9 mol. of mercuric acetate until a test portion gives no precipitate with ammonium sulphide. The solution is filtered whilst hot, and the mercurised acetate crystallises out on cooling. The mother-liquor from this, when treated with aqueous sodium chloride, yields the chloromercuri compound. Yields are quantitative. The substance forms small, yellow crystals, M.pt. 197° C. with decomposition, soluble in acetone and alcohol-acetic acid. The corresponding *chloride* is a yellow crystalline compound, melting with decomposition at 215° C., soluble in acetone or boiling alcohol.

p-Dimethylaminophenylmercuric acetate [2] may be obtained:

1. By the interaction of the amine and mercuric acetate at room temperature.

2. By dissolving yellow mercuric oxide in an aqueous solution of dimethylaniline acetate.

It crystallises in colourless, glistening needles, M.pt. 165° C., soluble in benzene, chloroform, or dilute acetic acid, insoluble in water. No mercuric sulphide is precipitated when it is treated with cold ammonium sulphide. Boiling with potassium iodide and subsequent passing of hydrogen sulphide only gives traces of mercuric sulphide.[3] The *hydroxide* is formed by the action of sodium hydroxide, and crystallises in microscopic prisms, turning brown at 150° C. and melting at 179° C. It is fairly soluble in warm water, the solution being feebly alkaline. On boiling the hydroxide with methyl iodide a *quaternary ammonium compound* is formed, $HgI.C_6H_4.NMe_3I$. This crystallises from boiling water in thin, flexible needles, which turn brown at 218° C. and melt at 230° C. on rapid heating. It is not attacked by boiling potassium hydroxide, but moist silver oxide yields the corresponding *base* as a caustic liquid, which rapidly absorbs carbon dioxide. The methiodide gives a *chloride* when treated in aqueous solution with silver chloride, which crystallises in small needles, soluble in water or alcohol. The latter yields a *double salt* with mercuric chloride, crystallising in laminæ, M.pt. 225° C. with decomposition.

The acetate with sodium chloride solution gives **p-dimethylaminophenylmercuric chloride**. The latter may also be obtained by shaking a benzene solution of p-mercuri-bis-dimethylaniline with a saturated benzene solution of hydrogen chloride, or from alcoholic p-mercuri-bis-dimethylaniline and mercuric chloride.[4] It crystallises from boiling alcohol in hexagonal plates, M.pt. 225° C., becoming red and decomposing. It is soluble in cold hydrochloric acid or chloroform,

[1] Kharasch and Jacobsohn, *J. Amer. Chem. Soc.*, 1921, 43, 1894.
[2] Pesci, *loc. cit.*; Dimroth, *Ber.*, 1902, 35, 2032.
[3] Dimroth, *Zeit. anorg. Chem.*, 1903, 33, 314.
[4] Michaelis and Rabinerson, *Ber.*, 1890, 23, 2342.

but less soluble in benzene. Warmed with sodium carbonate it yields dimethylaniline and mercuric chloride. The corresponding *bromide* melts at 226° C., and the *iodide* forms colourless plates, M.pt. 195° C. with decomposition.

p-Mercuri-bis-dimethylaniline.[1]

1. The p-bromodimethylaniline derived from 100 grams of dimethylaniline is dissolved in 70 grams of xylene, 1/10 the volume of ethyl acetate added, and sufficient 1·5 per cent. sodium amalgam to give double the quantity of sodium required for the reaction, and the mixture boiled for twenty-four hours. The mass is filtered and the filtrate distilled under reduced pressure, a faint yellow crystalline residue resulting, which changes to a white powder in contact with air.

2. By treating p-dimethylaminophenylmercuric chloride in pyridine with metallic copper. Yield 81 per cent.[2]

3. p-Dimethylaminophenylmercuric hydroxide in aqueous suspension is reduced by sodium sulphide, the product being extracted from the resulting precipitate by hot benzene.

It crystallises from benzene in needles containing benzene, this benzene of crystallisation being lost on standing in air. It is slightly soluble in alcohol or ether, but readily in chloroform, the crystals melting at 169° C. It is precipitated from its dilute hydrochloric acid solution by sodium hydroxide, but warming with hydrochloric acid leads to decomposition. It readily reacts with phosphorus trichloride to give dimethylamidophosphenyl chloride, $Cl_2P.C_6H_4.NMe_2$.

When 2 mols. of p-mercuri-bis-dimethylaniline in benzene solution are treated dropwise with a solution of thionyl chloride in the same solvent, a bright yellow product is precipitated. The reaction is represented as follows :—

$$2(C_6H_4NMe_2)_2Hg + SOCl_2 = (C_6H_4NMe_2)_3S.O.Hg.C_6H_4NMe_2 + HgCl_2.$$

This compound is decomposed by hydrogen sulphide, hexamethyltriamidotriphenylsulphine chloride being obtained.[3]

Methyl iodide reacts with p-mercuri-bis-dimethylaniline to form the *quaternary ammonium compound* $(C_6H_4.NMe_3I)_2Hg$, colourless crystals, becoming yellow at 218° C. and melting at 230° C. This yields the corresponding *chloride* with silver chloride, the mercuric chloride double salt of which decomposes at 225° C.

o-Acetoxymercuri-p-bromodimethylaniline.[4]—An alcoholic solution of p-bromodimethylaniline and an aqueous solution of mercuric acetate are mixed at 30° C., tightly stoppered in a bottle, and allowed to stand for six days. Needles separate out in 74 per cent. yield. If more concentrated solutions are used and heat is applied only a brown oil is obtained, which does not crystallise after standing for three months, and a lower yield also results when the mercuric acetate is slowly added with vigorous stirring. The acetate crystallises in white needles, M.pt. 144° C., very soluble in hot methyl alcohol or carbon disulphide, fairly soluble in hot ethyl acetate, benzene, carbon tetrachloride, or cold concentrated ammonium hydroxide, practically insoluble in water

[1] Pesci, *Gazzetta*, 1893, 23, ii. 521; Michaelis and Schlenk, *Ber.*, 1888, 21, 1501; *Annalen*, 1890, 260, 6.

[2] Hein, Wagler, and Retter, *Ber.*, 1925, 58, [B], 1507.

[3] Michaelis and Godchaux, *Ber.*, 1891, 24. 758.

[4] Whitmore, *J. Amer. Chem. Soc.*, 1919, 41, 1841.

or petroleum ether. No black mercuric sulphide is precipitated by ammonium sulphide. The following salts are also known :—

Chloride, from alcoholic solution of acetate by alcoholic calcium chloride; separates from alcohol or benzene in felted masses of needles, M.pt. 183° C. *Bromide*, forms larger crystals than the chloride and is more soluble; M.pt. 182° C. *Iodide*, much more soluble, M.pt. 169° C. *Thiocyanate*, fine white, gritty crystals, M.pt. 135° C., decomposing at 140° C. *Hydroxide*, from alcoholic acetate and the requisite amount of sodium hydroxide in alcohol, forms hard, warty masses of crystals, M.pt. 162° C. *Formate*, fine felted needles, M.pt. 145° C., decomposing at 150° C.

Mercuri-bis-p-bromodimethylaniline.—The acetate, 27·6 grams, is mixed with 23 grams of potassium iodide in 200 c.c. of alcohol, and the mixture heated under reflux for eight hours. The precipitate is filtered and extracted with cold benzene to remove impurities. Yield 15·5 grams, 86 per cent. Four crystallisations from benzene give fine, white needles, M.pt. 123° C., readily soluble in cold benzene, toluene, ether, acetone, or carbon disulphide. Smaller yields of this compound are also obtained from the above acetate by the action of sodium thiosulphate or potassium sulphide.

The mercuri-bis compound reacts with mercuric chloride, bromide, iodide, and thiocyanate, giving good yields of the above salts.

o-Nitro-p-acetoxymercuri-dimethylaniline.[1]—The preparation of this and the following compounds has been described under p-nitro-o-acetoxymercuri-monomethylaniline (p. 121). It is a bright yellow, crystalline substance, M.pt. 160° C., soluble in the usual organic solvents. With sodium chloride solution it yields the *p-chloro* derivative, a red amorphous product, M.pt. 185° C. with decomposition, soluble in acetone or boiling alcohol.

m-Nitro-p-acetoxymercuri-dimethylaniline occurs as brilliant orange needles, M.pt. 140° C., soluble in the usual solvents. The *chloride* is red and amorphous, M.pt. 220° C. with decomposition.

p-Ethylaminophenylmercuric acetate[2] forms colourless prisms, M.pt. 130° C., insoluble in water. Treated in alcoholic solution with calcium chloride, the *chloride* is obtained as hexagonal plates, M.pt. 143° C., soluble in boiling alcohol, but insoluble in water. The acetate reacts with potassium hydroxide to form the *hydroxide*, colourless needles, decomposing at 145° C., slightly soluble in cold water, insoluble in ether. This hydroxide with methyl iodide yields the *quaternary ammonium compound*, $HgI.C_6H_4.Et.NMe_3I$, which crystallises in long, colourless, glistening needles, M.pt. 202° C., easily soluble in hot water, and unchanged by caustic alkali. From this may be obtained the *chloride*, colourless needles, which form a double salt with mercuric chloride, M.pt. 169° C., and the *hydroxide*, which forms a highly caustic solution which absorbs carbon dioxide from the atmosphere.

p-Mercuri-bis-monoethylaniline is obtained by the action of sodium sulphide on the hydroxide. It crystallises from boiling xylene in colourless needles, M.pt. 166° C., whilst from alcohol or benzene it crystallises in plates.

p-Nitro-o-acetoxymercuri-monoethylaniline occurs as small yellow crystals from alcohol, M.pt. 183° C. The *chloride* is a yellow,

[1] Kharasch and Jacobsohn, *J. Amer. Chem. Soc.*, 1921, 43, 1894.
[2] Pesci, *Zeitsch. anorg. Chem.*, 1897, 15, 208.

DropBooks

amorphous solid, M.pt. 218° C. Both are soluble in alcohol or acetone.[1]

p-Diethylaminophenylmercuric acetate[2] forms colourless, glistening needles, M.pt. 104·4° C., soluble in alcohol, ether, or dilute acetic acid, insoluble in water. The *chloride* crystallises in thin needles, M.pt. 164·5° C., sparingly soluble in hot water, and when heated with aqueous sodium carbonate yields an *oxide*, $(Hg.C_6H_4.NEt_2)_2O$, crystallising in lustrous, colourless needles, M.pt. 220° C.[3] The *hydroxide* forms colourless needles, M.pt. 200° C. with decomposition, slowly decomposed by boiling water. When heated with methyl iodide in methyl alcohol solution it gives a *quaternary ammonium compound*, $(C_6H_4.NEt_2MeI)_2Hg$, small colourless prisms, M.pt. 203° C., slightly soluble in cold alcohol, insoluble in ether or benzene. The corresponding *chloride* crystallises in long, colourless needles, which yield a *double salt* with mercuric chloride, M.pt. 200° C. with decomposition.

p-Mercuri-bis-diethylaniline is prepared (1) from p-bromodiethylaniline and sodium amalgam, (2) from reduction of the hydroxide by sodium sulphide, (3) from the above oxide by the action of sodium thiosulphate. It crystallises in small, colourless prisms from hot benzene, M.pt. 160·6° C., soluble in ether, insoluble in alcohol. With methyl-iodide it gives the usual *quaternary ammonium compound*.

Derivatives of Benzylaniline.[4]

p-Benzylaminophenylmercuric acetate, obtained by the interaction of benzylaniline and mercuric acetate in aqueous alcohol at 50° C., forms colourless needles, M.pt. 143° to 144° C., soluble in benzene or chloroform, insoluble in water. The *chloride*, isolated in the usual way, is a powder, crystallising from benzene or alcohol in glistening plates, M.pt. 173° to 174° C. The *hydroxide* sinters at 82° C. and melts at 215° C., and is decomposed by alcohols or benzene. Treated with nitric acid the hydroxide gives a *nitrate*, a crystalline powder, decomposed by boiling water and melting with decomposition at 150° C.

p-Mercuri-bis-benzylaniline, prepared from the hydroxide by the action of aqueous sodium thiosulphate, crystallises from benzene in small, colourless needles, M.pt. 171° C. with partial decomposition. It is insoluble in methyl or ethyl alcohol.

Derivatives of Acid Anilides.[5]

p-Acetaminophenylmercuric acetate.—An intimate mixture of 2 mols. of mercuric acetate and 1 mol. of acetanilide is heated for one hour at 114° to 115° C., then for two hours at 100° C. Two volumes of boiling water are then added, and the mixture filtered after standing for twenty-four hours. It crystallises from boiling water in microscopic tetrahedra, M.pt. 220° C., soluble in boiling water, methyl, or ethyl

[1] Kharasch and Jacobsohn, *J. Amer. Chem. Soc.*, 1921, 43, 1894.

[2] Piccinini, *Gazzetta*, 1893, 23, ii. 534; Ruspaggiari, *Gazzetta*, 1893, 23, ii. 544; Pesci, *Zeitsch. anorg. Chem.*, 1897, 15, 208.

[3] Pigorini, *Gazzetta*, 1894, 24, ii. 465.

[4] Pesci, *Zeitsch. anorg. Chem.*, 1897, 15, 208.

[5] Pesci, *Gazzetta*, 1894, 24, ii. 449; *Zeitsch. anorg. Chem.*, 1897, 15, 222; *Chem. Zeit.*, 1899, 23, 58; *Chem. Zentr.*, 1899, i. 527; Piccinini, *Gazzetta*, 1894, 24, ii. 453.

alcohol, insoluble in benzene. The *chloride* crystallises with 2 mols. of water in microscopic needles which lose their water at 100° C. They melt at 250° C., are slightly soluble in alcohol, insoluble in water. The *hydroxide* is a micro-crystalline substance having a strongly alkaline reaction. It decomposes at 270° C., and with sodium or barium sulphides yields p-mercuri-bis-acetanilide. When the acetate is treated with sulphuric acid, a *sulphate* is obtained as colourless needles, soluble in acetic acid or alkali acetates, insoluble in water or alcohol.

p-Mercuri-bis-acetanilide, prepared as stated above, crystallises in colourless needles, M.pt. 244° to 246° C., and when heated with alcoholic potassium hydroxide at 100° C. in a sealed tube it yields p-mercuri-bis-aniline. The anilide is slightly soluble in boiling alcohol, but insoluble in other solvents.

Penta-acetoxymercuri acetanilide, $C_6.NHAc.(Hg.OAc)_5$.[1]—An intimate mixture of 16 grams of mercuric acetate and 1 gram of acetanilide is heated at 115° to 145° C. until a test portion gives no reaction for mercury ions. The product is dissolved in ammonium hydroxide, acetic acid added, and in twenty-four hours needles are deposited. These dissolve in cold water, the solution being viscous, and when heated to 80° C. coagulation takes place. When treated with bromine, penta-bromacetanilide, M.pt. 284° to 285° C., is obtained.

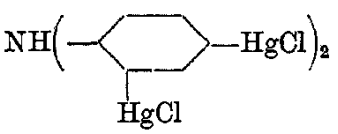
Derivatives of Diphenylamine.

p-Acetoxymercuri-diphenylamine, $C_6H_5.NH.C_6H_4.Hg.OAc$.[2]—An alcoholic solution of diphenylamine is treated with a solution of mercuric acetate in 50 per cent. alcohol in the presence of a little acetic acid. The acetate crystallises from alcohol in plates, M.pt. 178° C., slightly soluble in alcohols or hot benzene, insoluble in water. Treated with alcoholic calcium chloride it gives the *chloride*, microscopic plates, decomposing above 240° C.

With potassium hydroxide the *hydroxide* is formed, a white, amorphous substance decomposing above 200° C. It has an alkaline reaction in aqueous and alcoholic solution.

p-Mercuri-bis-diphenylamine, obtained from the hydrate by sodium thiosulphate, is a white powder. It crystallises in scales from boiling benzene or chloroform, M.pt. 182·5° C.

2 : 2′ : 4 : 4′-Tetrachloromercuri-diphenylamine,[3]



Diphenylamine and mercuric chloride are heated together, and the melt poured into acetic acid and boiled for some time. A yellow product is obtained, from which unchanged diphenylamine is removed by extraction with acetic acid. It does not melt at 260° C., and is insoluble in all organic solvents.

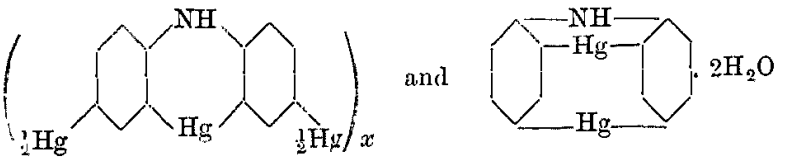
When boiled with pyridine the compound appears to be decomposed

[1] Raffo and Rossi, *Zeitsch. Chem. Ind. Kolloide.*, 1912, 11, 120; *Chem. Zentr.*, 1912, ii. 2070; Bernardi, *Gazzetta*, 1926, 56, 337.

[2] Prussia, *Gazzetta*, 1898, 28, ii. 129; *Chem. Zentr.*, 1898, ii. 928.

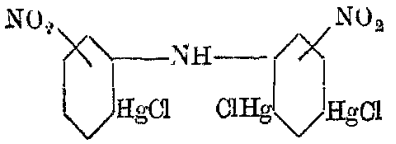
[3] Kharasch and Piccard, *J. Amer. Chem. Soc.*, 1920, 42, 1855.

into mercuric chloride and **3 : 3'-mercuri-mercazine**, to which the following formulæ have been assigned :—

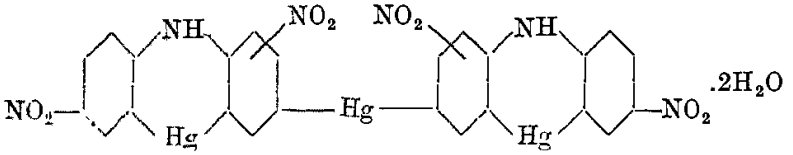


This compound, with sodium thiosulphate in alcoholic solution at 70° C., yields a grey product insoluble in all organic solvents. It is unstable towards nitric acid, and when heated to 100° C. *in vacuo* mercury distils off.

Nitration of the tetrachloromercuri compound by mixed acid gives a light brown compound, insoluble in organic solvents, but partly soluble in sodium hydroxide, giving a red coloration. The position of the nitro groups is uncertain, and the following structure is given :—



This compound, when treated with sodium thiosulphate, gives a light brown substance, which loses mercury at 100° C. *in vacuo*, and when heated at 54° C. *in vacuo* for fifteen minutes loses 5·22 per cent. of water. The name, **mercury-bis-3-dinitro(?)-mercazine**, has been assigned to it, and the following structure :—



p-Acetoxymercuri-methyldiphenylamine,[1] prepared in the usual manner, crystallises from alcohol in needles, which yield the *hydroxide* when treated with potassium hydroxide, as a white amorphous powder.

p-Mercuri-bis-methyldiphenylamine is isolated from the acetate by treatment with 25 per cent. sodium thiosulphate. It crystallises from benzene-ligroin in colourless plates, M.pt. 138° to 139° C.

Acetoxymercuri-N-methylthiodiphenylamine[2] is obtained when N-methylthiodiphenylamine in alcohol or acetic acid is treated with mercuric acetate. A *diacetoxymercuri* derivative is also produced at the same time. The former compound melts at 165° C., the latter decomposes without melting at 300° C. If the N-methylthiodiphenylamine be replaced by thiodiphenylamine no mercury derivative results, but only o-dithiotetraphenylhydrazine, this product also occurring on the interaction of mercury acetamide and thiodiphenylamine.[3]

Derivatives of α-Anilido Fatty Acids and their Esters.[4]

In this series of compounds the substitution of mercury becomes more easy as the series is ascended. Whilst the ethyl α-anilido acetate

[1] Garbarini, *Gazzetta*, 1898, 28, ii. 132; *Chem. Zentr.*, 1898, ii. 928.
[2] Finzi, *Giorn. Chim. Ind. Appl.*, 1927, 9, 176.
[3] Pesci, *Gazzetta*, 1916, 46, i. 103.
[4] Schoeller, Schrauth, and Goldacker, *Ber.*, 1911, 44, 1300; German Patent, 248291.

forms only a mono-substitution product, the propionic ester gives a mixture of mono- and di-substitution products. In the case of the butyric and isovaleric esters, only di-substituted products of the type $C_6H_3.(Hg.OAc)_2.NH.CHR.CO_2Et$ are obtained.

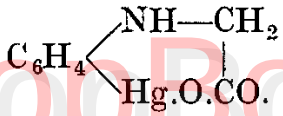
2-Acetoxymercuriphenylglycine ethyl ester,

$$OAc.Hg.C_6H_4.NH.CH_2.CO_2Et.$$

Ten grams of the pure phenylglycine ester in 50 c.c. of methyl alcohol are treated with a solution of 20 grams of mercuric acetate in 50 c.c. of water, the mixture being stirred during the addition. A further quantity of methyl alcohol is added, and in fifteen minutes pale yellow crystals commence to separate. After twenty-four hours these are filtered off and washed with water, the yield of crude product being 20 grams, 82 per cent. It is recrystallised from chloroform, small tabular crystals being obtained. These soften at 129° C. and melt at 132° C. When bromine or iodine in their respective alkali halides are added to the ester, the acetoxymercuri group is replaced by halogen.

2-Chloromercuriphenylglycine ethyl ester.—The above acetate is treated with sodium chloride in aqueous alcohol solution. It crystallises in needles or rhombic plates, sintering at 150·5° C. and melting at 152·5° C. The corresponding *bromide* forms rhombic plates, sintering at 144° C., M.pt. 147·5° C.; the *iodide*, lustrous leaflets, sintering at 137° to 138° C., M.pt. 139° to 140° C.

2-Hydroxymercuriphenylglycine anhydride,



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This product is obtained by saponifying the acetate by 1·25 mols. of Normal sodium hydroxide solution, and acidifying the resulting solution with Normal sulphuric acid. Yield 91 per cent. It is decomposed at 228° C. (corr.). When dissolved in the calculated quantity of Normal alkali it gives precipitates with the salts of various metals: the copper salt is light green, decomposing at 193° to 197° C.; lead, iron, calcium, silver, mercury and platinum salts are also known.

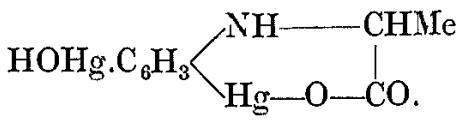
(2-Chloromercuriphenyl-α-amino) propionic ethyl ester, $ClHg.C_6H_4.NH.CHMe.CO_2Et$.—Equimolecular quantities of mercuric acetate and the ester are allowed to react in aqueous methyl alcohol solution. A 68 per cent. yield of the acetate is obtained, which is contaminated with dimercuri ester. It is soluble in organic solvents and precipitated as a yellow oil by light petroleum. Standing in ice for twelve hours does not induce solidification, so that the oil is treated with sodium chloride and converted to the chloro compound. This crystallises from 80 per cent. alcohol in microscopic needles, M.pt. 165·5° C. Yield 80 per cent.

(2:4-Diacetoxymercuri-α-amino) propionic ethyl ester.—To 10 grams of the anilido ester in 10 c.c. of methyl alcohol, 35 grams of mercuric acetate in 100 c.c. of water and 80 c.c. of methyl alcohol are gradually added with constant stirring. The reaction is complete in an hour. The product is left overnight in ice, then filtered and washed with cold water. Yield 30 grams, 80 per cent. It is soluble in the usual solvents, and completely soluble in 10 per cent. acetic acid without splitting off the mercury. The above product contains a *crystalline* and an

amorphous form of the diacetate, the former being soluble in hot methyl alcohol containing acetic acid, and both give the same substance when treated with alkali halides.

(2 : 4-Dichloromercuriphenyl-α-amino) propionic ethyl ester is prepared from the above compound by the addition of aqueous sodium chloride. It crystallises from ethyl acetate—ligroin in small needles, sintering at 128° C. and melting at 131° C. (corr.). The corresponding *dibromide* forms needles, M.pt. 128·5° C. (corr.).

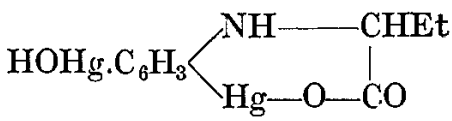
(2 : 4-Dihydroxymercuriphenyl-α-amino) propionic anhydride.



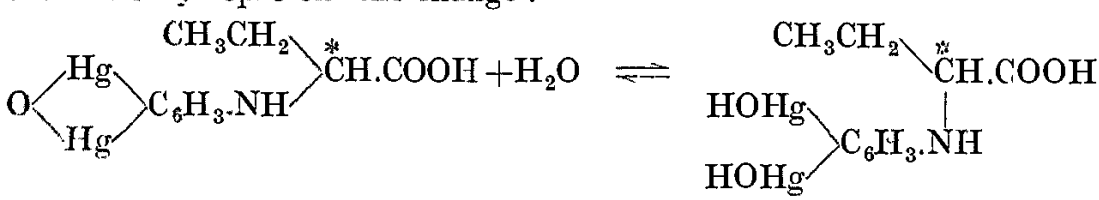
This is obtained by hydrolysis of the diacetate, using aqueous sodium hydroxide. It readily absorbs water and decomposes at 223° C. (corr.).

(2 : 4-Diacetoxymercuriphenyl-α-amino) butyric ethyl ester, $(Hg.OAc)_2C_6H_3.NH.CHEt.CO_2Et$.—This is prepared in the usual manner, with 82·3 per cent. yield. It crystallises in stout rods, sintering at 150° C. and melting at 154·5° C. (corr.). It is readily soluble in alcohols or chloroform, but only slightly in other solvents. With sodium chloride it yields the *dichloro compound*, slender needles, M.pt. 127° C. (corr.), and the corresponding *dibromo derivative* forms needles, sintering at 125° C., M.pt. 127° C. (corr.); the *di-iodide* forms needles, M.pt. 120° C. (corr.).

(2 : 4-Dihydroxymercuriphenyl-α-amino) butyric anhydride,



is obtained in 90 to 92 per cent. yield by saponification of the diacetoxy ester with 3·25 mols. of Normal sodium hydroxide. It becomes yellowish-brown at 200° C. and decomposes at 209° C. (corr.). It readily takes up moisture on exposure to the air and the following scheme may represent the change :—



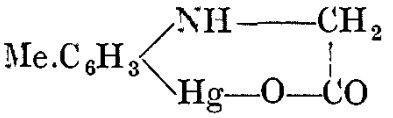
(2 : 4-Diacetoxymercuriphenyl-α-amino) isovalerianic ethyl ester.—The reaction is complete in thirty minutes, an 86 per cent. yield being obtained. It crystallises in stellar aggregates of needles, M.pt. 126° C. (corr.). The *dichloro compound* forms microscopic rods, M.pt. 122° C. (corr.), and the *dibromide* occurs in *two forms*: (*a*) a granular, sandy, amorphous modification, decomposing at 215° C. and insoluble in ethyl acetate; (*b*) a soluble form, white needles, M.pt. 135° C. (corr.); the *di-iodide* crystallises in yellow needles, M.pt. 129° C. (corr.). The *anhydride* is obtained in 90 per cent. yield, decomposes at 226° C. (corr.), and readily takes up moisture on exposure to the atmosphere.

Derivatives of Tolylglycine Esters.

Acetoxymercuri-o-tolylglycine ethyl ester, $AcO.Hg.C_6H_3Me.NH.CH_2.CO_2Et$.—The ester and mercuric acetate in methyl alcohol

give a 77 per cent. yield of this compound. It is soluble in methyl or ethyl alcohol, ethyl acetate, chloroform, acetone, ammonium hydroxide, or dilute acids; insoluble in light petroleum. It melts at 125·5° C. (corr.).

Hydroxymercuri-o-tolylglycine anhydride,



is obtained in 93 per cent. yield by saponification of the above acetate. It is insoluble in water or organic solvents, but easily soluble in alkali.

Diacetoxymercuri-o-tolylglycine ethyl ester is prepared in the usual manner, using 2 mols. of mercuric acetate. It forms slender needles, M.pt. 167° C. (corr.), difficultly soluble in alcohol, but readily in ammonium hydroxide. It is saponified by hot alkali.

Acetoxymercuri-m-tolylglycine ethyl ester, M.pt. 127·5° C. (corr.), yields a yellow *anhydride* on saponification.

Triacetoxymercuri-m-tolylglycine ethyl ester is formed in 20 per cent. yield when 3 mols. of mercuric acetate are used. It melts at 185° C. (corr.), is readily soluble in ammonium hydroxide, with difficulty in alcohol, and insoluble in the usual solvents.

Acetoxymercuri-p-tolylglycine ethyl ester, M.pt. 140° C. (corr.), yields an amorphous *anhydride* on saponification.

Derivatives of Toluidines and Toluidides.[1]

The mercuration of o-toluidine in methyl alcohol solution gives rise to a mono and a dimercurated compound, the latter forming 85 per cent. of the product. When 50 per cent. ethyl alcohol is used as the solvent the main yield is the monomercuri derivative.[2] If the reaction be carried out in aqueous solution, only a dimercurated product is obtained, which is isomeric with the one isolated from methyl alcohol solution.[3]

5-Acetoxymercuri-o-toluidine.—A solution of o-toluidine (3 mols.) in ethyl alcohol is rapidly added to a 50 per cent. alcoholic solution of mercuric acetate (1 mol.). The product is recrystallised first from 50 per cent. alcohol, then from absolute alcohol, any dimercuri compound being insoluble in the latter solvent. It is soluble in hot water or alcohol, less so in ethyl acetate, and melts at 144° to 145° C.

When treated with sodium chloride solution the *5-chloromercuri compound* is obtained. It crystallises from absolute alcohol in needles, M.pt. 178° C. Its *diacetyl* derivative forms colourless leaflets, M.pt. 170° C.

Diacetoxymercuri-o-toluidine.—(*a*) From methyl alcohol solution.

A solution of 37 grams of mercuric acetate in 100 c.c. of methyl alcohol is stirred into 10 grams of o-toluidine in 50 c.c. of methyl alcohol, and in a few minutes no mercury ions can be detected in the solution. After several hours the crystallisation of the diacetoxy compound commences. The small microscopic needles are allowed to stand in ice for forty-eight hours, then filtered, washed with alcohol, and dried at

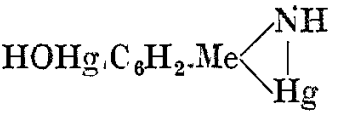
[1] Schrauth, Schoeller, and Rother, *Ber.*, 1912, 45, 2808.
[2] Jacobs and Heidelberger, *J. Biol. Chem.*, 1915, 20, 513.
[3] Vecchiotti, *Gazzetta*, 1926, 56, 155. See Rossi and Bocchi, *Gazzetta*, 1925, 55, 93.

100° C. Yield 21 grams, 73 per cent. It crystallises from methyl alcohol in microscopic needles, M.pt. 228° C. with decomposition, is insoluble in most organic solvents, slightly soluble in methyl alcohol, but readily soluble in acids, ammonium hydroxide, amines, ethylenediamine, or pyridine.

(*b*) From aqueous solution.

When equimolecular quantities of mercuric acetate and o-toluidine react in aqueous solution, the resulting diacetate melts at 208° C. The position of the acetoxy mercuri groups has not been determined, but they are apparently not 3 : 5 or 4 : 6.

Dihydroxymercuri-o-toluidine.—The diacetate (M.pt. 228° C.) in 30 parts of water at 80° to 90° C. is treated with an excess of sodium hydroxide, and on cooling the dihydroxymercuri compound separates in long, colourless needles. These when heated at 100° C. lose water, giving an infusible canary-yellow substance which blackens when heated and probably has the constitution :



The *hydroxide* obtained from the diacetate (M.pt. 208° C.) melts at 235° C. The *acetate* (M.pt. 228° C.) when treated in the usual manner yields a *chloride, bromide, iodide,* and *hydroxide*; the acetate (M.pt. 208° C.) gives the following derivatives : *chloride,* decomposes at 221° C.; *bromide,* decomposes at 232° C.; *acetotoluidide,* sinters at 214° C., M.pt. 219° C.; *hydroxide,* M.pt. 235° C.

Acetoxymercuri-aceto-o-toluidide.—Ten grams of o-aceto-toluidide in 250 c.c. of hot water are treated with 20 grams of mercuric acetate and the mixture boiled for forty minutes, then filtered whilst hot. It is then cooled in ice for twenty-four hours, the solution yielding 7 grams of needles, 28 per cent. yield. After recrystallisation from 80 per cent. alcohol, the needles melt at 233° C. (corr.). With iodine it gives 5-iodo-aceto-o-toluidide. Treatment with sodium chloride solution yields the *chloromercuri-aceto-o-toluidide,* M.pt. 167° C., which may also be obtained by acetylation of the chloromercuri-o-toluidine.

Diacetoxymercuri-aceto-o-toluidide.—Diacetoxymercuri-o-toluidine is dissolved in ethyl acetate and acetylated by means of acetic anhydride. The product melts at 240° C., and by double decomposition the following are obtained : *chloride*; *bromide,* microscopic needles; *iodide,* precipitated in flocks, which gradually change to a crystalline modification on standing. The acetate with iodine gives long, silky needles, M.pt. 222·5° C. (corr.), which contain no mercury.

6-Acetoxymercuri-m-toluidine crystallises in small needles, M.pt. 176° C., and **2 : 5-diacetoxymercuri-m-toluidine** forms white needles, M.pt. 170° C., these yielding an *hydroxide,* decomposing at 200° C.; a *chloride,* decomposing at 239° to 240° C.; a *bromide,* decomposing at 150° C.

Diacetoxymercuri-m-toluidine (1 : 3 : 4 : 6)[1] crystallises in white plates, M.pt. 191° C.; the *hydroxide* is not very stable; the *chloride* and *bromide* crystallise in plates, melting at 195° C. and 210° C. respectively.

Triacetoxymercuri-m-toluidine.—Three grams of m-toluidine and 27 grams of mercuric acetate in 85 c.c. of methyl alcohol gave

[1] Vecchiotti, *Gazzetta,* 1924, 54, 411.

23 grams of crystals after two days' standing. Yield 95·3 per cent. It forms bright yellow microscopic crystals, insoluble in the usual organic solvents, but soluble in ammonium hydroxide.

Acetoxymercuri-aceto-m-toluidide may be obtained from an aqueous solution of mercuric acetate and the toluidide by heating for one hour. Yield 20 per cent. It gives crystals from 30 per cent. alcohol, M.pt. 99° C.

If the above diacetoxy compound is acetylated, *diacetoxymercuri-aceto-m-toluidide* is formed. It is insoluble in organic solvents, slightly soluble in hot water, and easily soluble in ammonium hydroxide. With iodine 4 : 6-di-iodoaceto-m-toluidide is obtained. In a similar manner the triacetoxymercuri compound yields a *toluidide*, as a heavy insoluble powder.

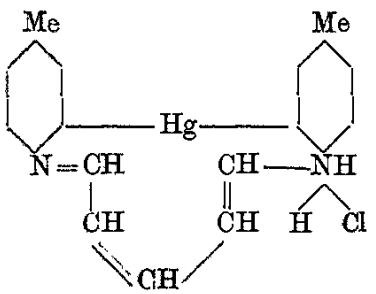
Diacetoxymercuri-aceto-m-toluidide, prepared from the 1 : 3 : 4 : 6 compound, forms tufts of needles, M.pt. 250° C., and may be converted to 4 : 6-dibromo-aceto-m-toluidide; 6-*acetoxymercuri-aceto-m-toluidide* melts at 192° C. and yields 6-bromoaceto-m-toluidide; 2 : 5-*diacetoxymercuri-aceto-m-toluidide* forms silky, white needles, M.pt. 183° to 184° C.

Acetoxymercuri-p-toluidine.[1]—The reaction is carried out in 50 per cent. alcohol, and occupies two days. The product is purified by dissolving it in a mixture of ammonium acetate and hydroxide and adding acetic acid. It melts at 184° C., is insoluble in water, slightly soluble in alcohol, ether, or benzene.

With calcium chloride in alcoholic solution it gives the *chloride*, prismatic crystals, M.pt. 170° C., insoluble in water, only slightly soluble in alcohol.[2] The *hydroxide* crystallises from a solution of the acetate in concentrated potassium hydroxide in yellowish plates, M.pt. 212° to 213° C. It is insoluble in the usual solvents.

Mercuri-bis-p-toluidine is obtained from the preceding hydroxide, by the action of concentrated sodium thiosulphate. It crystallises in plates, M.pt. 156° C.

Condensation with Dinitrophenylpyridinium chloride.[3]—The pyridine compound (1 mol.) in methyl alcohol is added to the mercurated toluidine (1 mol.) in pyridine solution. A deep red coloration takes place on mixing and the whole is boiled for about thirty minutes. Then a slight excess of dilute hydrochloric acid is added to remove the pyridine, and the precipitate washed with boiling acetone to remove any dinitraniline. The pure substance is a brown powder, M.pt. 133° C., soluble in chloroform. Formula :



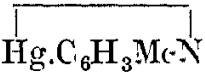
Hydroxymercuri-aceto-p-toluidide anhydride is obtained from

[1] Vecchiotti, *Gazzetta*, 1921, 51, ii. 208; Pesci, *Gazzetta*, 1898, 28, ii. 445; *Chem. Zentr.* 1898, ii. 546; *Zeit. anorg. Chem.*, 1898, 17, 276.

[2] See Klein, *Ber.*, 1878, 11, 743.

[3] Reitzenstein and Stamm, *J. prakt Chem.*, 1910, [2], 81, 150.

the toluidide and mercuric acetate in aqueous solution. It crystallises in leaflets, M.pt. 229° C. (corr.). Formula :



Acetoxymercuri dimethyl-p-toluidine[1] crystallises from boiling benzene in colourless, slender, glistening needles, M.pt. 131·5° C., insoluble in water, more soluble in methyl than ethyl alcohol.

The following compounds are obtained from the acetate in the usual manner :—

Chloride, very fine needles, M.pt. 159° to 159·5° C., soluble in benzene, insoluble in water. *Bromide*, colourless, glistening needles, M.pt. 149° to 150° C. *Iodide*, needles, M.pt. 126° C. *Nitrate*, using alcoholic calcium nitrate, colourless needles, M.pt. 131° C., soluble in alcohol or benzene. *Hydroxide*, obtained by allowing acetate to stand with concentrated potassium hydroxide for twenty-four hours; colourless needles, M.pt. 117° C., fairly soluble in hot water, slightly soluble in benzene or methyl alcohol.

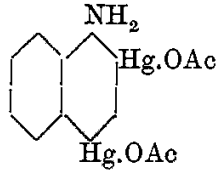
Mercuri-bis-(dimethyl-p-toluidine) is obtained when the above hydrate is treated with concentrated sodium thiosulphate, and when bromo-dimethyl-p-toluidine is heated with 1·5 per cent. sodium amalgam for forty-eight hours at 120° to 125° C., a little ethyl acetate being used as catalyst. It crystallises in colourless, glistening plates. M.pt. 60° C., slightly soluble in benzene.

Derivatives of Benzidine.

3(?)-Acetoxymercuri-benzidine.[2]—This compound appears to be formed when benzidine and mercuric acetate react in glacial acetic acid. It is a brown product, decomposing at 138° to 140° C., and forming a *hydrochloride*, M.pt. 239° to 240° C. Diacetylbenzidine and mercuric acetate when heated at 120° to 160° C. give a crystalline *compound*, $C_{52}H_{30}O_4N_4Hg,3H_2O$, which seems to be of indefinite composition.

Derivatives of the Naphthylamines and their Sulphonic Acids.[3]

2 : 4-Diacetoxymercuri-α-naphthylamine,



α-Naphthylamine (4·2 grams) is dissolved in a mixture of 20 c.c. of alcohol and 20 c.c. of acetic acid, then 50 c.c. of boiling water are added. To this hot solution, a hot solution of 10 grams of mercuric acetate in 50 c.c. of water is added. An intense yellow precipitate is formed; this gradually becomes white and crystalline, and is filtered off. Yield 9·5 grams. The substance is coloured faint yellow by sodium hydroxide, but does not react with ammonium sulphide even on long standing. It

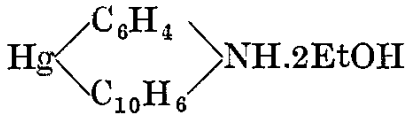
[1] Pesci, *Gazzetta*, 1898, 28, ii. 445.
[2] Bernardi and Tartarini, *Gazzetta*, 1927, 57, 223.
[3] Brieger and Schulemann, *J. prakt. Chem.*, 1914, 89, 140.

is very stable towards halogen salts. No monomercuri derivative is isolated.

Tetra-acetoxymercuri-α-acetonaphthalide, $NHAc.C_{10}H_3(Hg.OAc)_4$,[1] from α-acetonaphthalide and 4 mols. of mercuric acetate, decomposes at 220° C., and forms aqueous solutions which froth when shaken, are highly viscous, and coagulate when heated.

1-Acetoxymercuri-β-naphthylamine.—β-Naphthylamine (1·4 grams) and 3·2 grams of mercuric acetate in 25 c.c. of dilute acetic acid yield colourless crystals. These become intense yellow without dissolving when treated with concentrated sodium hydroxide, and ammonium sulphide readily reacts with the acetate.

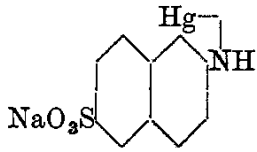
Mercuriphenyl-β-naphthylamine,



is formed by treating phenyl-β-naphthylamine with dilute alcoholic mercuric acetate containing a little acetic acid. It melts at 173° C.,[2] and crystallises with 2 mols. of alcohol.

β-Naphthylamine-6-sulphonic acid Derivatives.[3]—The sodium salt of this acid in aqueous solution reacts with aqueous mercuric acetate if the compounds are allowed to stand for a long time. A white product is obtained, which gives mercuric oxide when treated with sodium hydroxide. If the reaction mixture is boiled for five to ten minutes, a white body is again obtained, but this does not react with sodium hydroxide. It is insoluble in all solvents. To these two bodies the following formulæ have been assigned :—

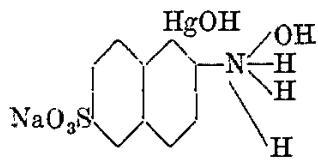
Sodium naphthylamine sulphonate (5·6 grams) is dissolved in 125 c.c. of boiling water, and a solution of 6·4 grams of mercuric acetate in 25 c.c. of water is poured in. The mixture is boiled for a few minutes, then sodium hydroxide is added dropwise until complete solution is obtained. The whole is then quickly cooled to 70° C. and 150 c.c. of alcohol added, a yellow body being precipitated. The whole is cooled quickly, shaken, and filtered, the residue washed with 50 per cent. alcohol, absolute alcohol, and finally with ether. A pale yellow powder is obtained which corresponds to the formula :



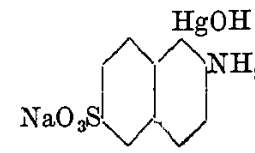
A pure white product is obtained from this by the action of an excess of sodium hydroxide. This product is soluble in water, aqueous alcohol, and dilute alkali. It does not react in aqueous solution with ammonium

[1] Rossi and Bocchi, *Gazzetta*, 1926, 56, 817.
[2] Rossi and Cecchetti, *Gazzetta*, 1925, 55, 869.
[3] Brieger and Schulemann, *loc. cit.*

sulphide, but with acetic acid a white precipitate is thrown out. This latter reacts with ammonium sulphide, and contains 1 mol. of water which cannot be removed by drying over phosphorus pentoxide, hence formula I. has been assigned to it, although analysis points to II. Thus:



I.

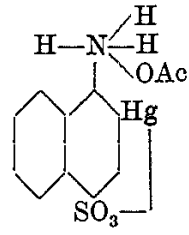


II.

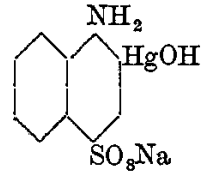
These mercurated naphthylamine sulphonic acids react immediately with halogen halides, the mercury being freed, and in the case of potassium iodide solution mercuric iodide separates.

Monomethylaminonaphthalene- and β-dimethylaminonaphthalene-6-sulphonic acids only reduce mercuric acetate to mercurous salt or metallic mercury.

Naphthionic acid Derivatives.—By the interaction of the sodium salt of this acid and mercuric acetate in the cold, a white, finely divided precipitate is obtained. When this is boiled it becomes soluble in sodium acetate and acetic acid. It crystallises from the latter as a *colourless body, which is only slightly affected by sodium hydroxide,* and only slowly attacked by ammonium sulphide. The following formula has been ascribed to it :—[1]



From a solution of 6·4 grams of sodium naphthionate and 6·4 grams of mercuric acetate in 150 c.c. of water, treated with a large excess of sodium hydroxide, a colourless product is obtained. This does not react with ammonium sulphide, and towards halogen salts it reacts similarly to hydroxymercuri-β-naphthylamine-6-sulphonic acid (sodium salt). When dried over phosphorus pentoxide the body becomes canary yellow, and on addition of water becomes white again. It has been formulated as the *sodium salt* of *2-hydroxymercuri-naphthionic acid.*

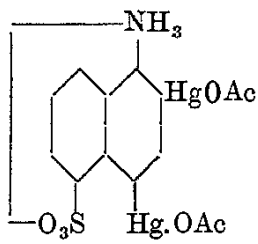


Using an excess of mercuric acetate does not produce dimercurated derivatives, the yellow solution becoming yellow-red on addition of alkali, but the colour is less intense than in the case of β-naphthylamine sulphonic acid.

1 : 5-Naphthylamine sulphonic acid Derivatives.—The free acid (2·4 grams) is dissolved in 25 c.c of water containing a little sodium

[1] Whitmore, *Organic Compounds of Mercury,* Chemical Catalog. Co., prefers to consider the compound to be 2-acetoxymercuri-naphthionic acid.

hydroxide, then dilute acetic acid is added until the solution is just acid. A solution of 6·4 grams of mercuric acetate in 25 c.c. of water is poured in, and a fine canary-yellow precipitate is deposited. This is soluble in acetic acid, and becomes deep yellow when treated with sodium hydroxide, but excess of hydroxide yields no precipitate, but tends to decompose the substance, mercurous oxide separating out. The yellow product does not react with ammonium sulphide. The body is very reactive with halogen salts, the addition of sodium chloride to its solution, followed by ammonium sulphide, causes blackening at once. With potassium iodide the reaction is quantitative, and with potassium bromide nearly so. The substance is represented by the structure :



DropBooks

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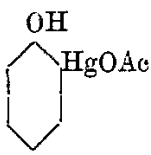
CHAPTER VIII.

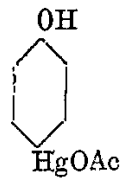
MERCURY (*continued*).

Derivatives of Aromatic Compounds containing Hydroxyl Groups.

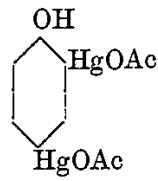
Most of the monohydric phenols and their substitution products react with mercuric acetate under suitable conditions to give acetoxymercuri compounds. When phenol is treated with an aqueous solution of mercuric acetate at room temperature, three products are formed:



I.



II.

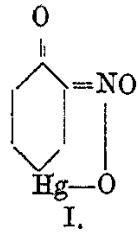


III.

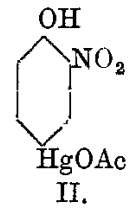
If, however, the reaction is carried out at 100° C., and no solvent used, only I. and II. are formed.

The methyl and ethyl ethers of phenol are more difficult to mercurate than phenol itself, and although ortho- and para-substituted monomercurated products can be made, no dimercurated derivatives are yet known.

The nitrophenols differ from all other phenols, in that they are capable of forming anhydrides instead of acetoxymercuri derivatives when treated with mercuric acetate. When, for example, the sodium salt of o-nitrophenol is shaken with aqueous mercuric acetate, it yields compound I.; but if the nitrophenol is dissolved in warm water containing a little sodium hydroxide, and the mercuric acetate solution added dropwise, compound II. is produced.



I.



II.

Compound I. gives the corresponding chloride and hydroxide when treated with hydrochloric acid and sodium hydroxide respectively, but bromine, or iodine in potassium iodide solution, replace the mercury by halogen. p-Nitrophenol is more difficult to mercurate than the ortho compound, and the reagents have to be boiled for a long period.

4 : 6-Dinitrophenol is mercurated by boiling for sixteen hours with

mercuric oxide in aqueous solution, but picric acid yields a product when shaken with aqueous mercuric oxide for several hours at 80° C.

Dimethylaminophenol readily reacts with mercuric acetate in alcoholic solution, the operation going to completion in two minutes at 100° C., but the compound formed slowly decomposes when kept. If, however, no solvent is used, no organic mercury derivative is formed. A rather unstable body containing two benzene nuclei connected by a mercury bridge is formed from m-hydroxyphenyltrimethylammonium acetate, but its aqueous solution decomposes in a week.

In the same way that the phenolic ethers are more difficult to mercurate than the phenols themselves, so cresol methyl ether is less readily attacked by mercuric acetate than cresol, and requires five days' heating at 50° C. to complete the reaction, a diacetoxymercuri compound only being produced.

Thymol and carvacrol yield mono or dimercurated products according to the number of molecules of mercuric acetate used in the reaction.

Safrol, eugenol methyl ether, apiol and isoapiol yield a mixture of two isomeric acetates, one of which is crystalline, the other syrupy.

Other methods have also been used for producing mercurated anisoles and phenetoles of the type RHgX. (1) The type R_2Hg, *e.g.* mercury dianisyl, is treated with an alcoholic solution of mercuric chloride. (2) The mercuric chloride addition products of the triarylstibines, $R_3Sb.HgCl_2$, are boiled in alcoholic solution.

The R_2Hg compounds of the phenols are prepared by the usual methods, mercuri-bis-o-phenol being formed by the action of sodium thiosulphate on o-chloromercuri phenol, whilst the anisyl and phenetyl compounds are formed either by treating o-bromoanisole or phenetole with 1·5 per cent. sodium amalgam or by the action of alcoholic potassium iodide on o-iodomercuri anisole or phenetole.

DropBooks

The following evidence has been collected to show the behaviour of mercurated phenols towards acids, bases, and salts:—

o-Chloromercuri phenol in sodium hydroxide solution, when treated with sodium nitrite at −4° to −5° C., and the mixture acidified with concentrated sulphuric acid, yields p-nitrosochloromercuriphenol; the latter when heated with a mixture of ammonium chloride, acetate, and carbonate for thirty minutes at 100° C. is transformed into p-nitroso-o-chloromercuri aniline.

p-Chloromercuri phenol is decomposed when boiled with hydrochloric acid, giving mercuric chloride and phenol, but with ethereal iodine solution, mercuric iodide and p-iodophenol result.

Chloromercuri anisole and phenetole yield oxides when treated with aqueous sodium carbonate solution, *e.g.* $O(HgC_6N_4OMe)_2$.

4-Acetoxymercuri-m-dimethylaminophenyl acetate is immediately decomposed by ammonium sulphide.

Acetoxymercuri-p-cresol does not yield the corresponding iodide when treated with potassium iodide, but the mercury is eliminated as mercuric iodide. Chloromercuri-p-cresol in alcoholic solution gives the anhydride of hydroxymercuri-p-cresol when a boiling sodium carbonate solution is added. The diacetoxymercuri derivative of p-cresol methyl ether is stable towards ammonium hydroxide or sulphide, but gives the chloride on the addition of aqueous sodium chloride.

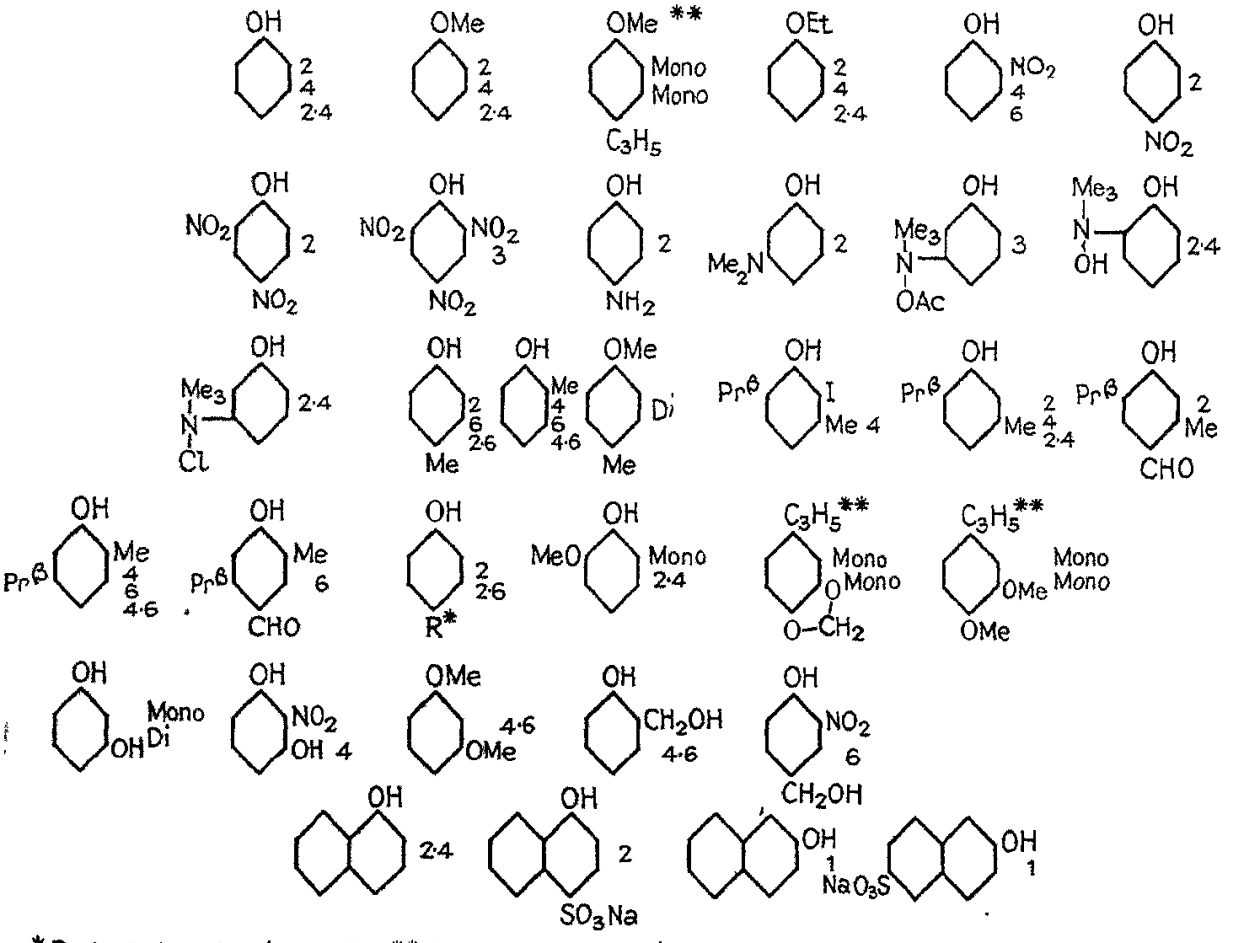
The crystalline chloromercuri compound obtained from safrol is stable towards ammonium sulphide or ammonium and sodium hydroxides,

but decomposed when boiled with dilute hydrochloric acid. The corresponding iodomercuri derivative, however, is decomposed by hydrogen sulphide. Similar reactions have been noted with the crystalline chloride of eugenol methyl ether.

Chloromercuri resorcinol is readily decomposed by sodium hydroxide and immediately by ammonium sulphide, and the dichloromercuri resorcinol is even less stable to sodium hydroxide. Diacetoxymercuri resorcinol dimethyl ether does not give mercuric sulphide with ammonium sulphide, but only a yellow precipitate.

The stability of the mercurated α-naphthols towards alkali halides decreases from the chlorides to the iodides, potassium iodide eliminating the mercury as mercuric iodide. Diacetoxymercuri-α-naphthol is stable to ammonium sulphide. 2-Acetoxymercuri-1:4-naphthol monosulphonic acid is very stable towards ammonium sulphide, but when warmed with sodium chloride in acetic acid solution, mercury is split out, and 1-acetoxymercuri-2:6-naphthol sulphonic acid has similar properties. 1-Acetoxymercuri-β-naphthol is not blackened by cold ammonium sulphide, but gives mercuric sulphide on heating.

The following table shows the positions taken up by mercury on entering the benzene nucleus. All rings are numbered from the top (position 1) in a clockwise direction, irrespective of the group occupying that position. This method of numbering applies only to the table and not to the text.


OH 2 4 2·4
OMe 2 4 2·4
OMe ** Mono Mono C3H5
OEt 2 4 2·4
OH NO2 4 6
OH 2 NO2
OH NO2 2 NO2
OH NO2 NO2 3 NO2
OH 2 NH2
OH 2 Me2N
OH Me3 N 3 OAc
Me3 N OH OH 2·4
OH Me3 N Cl 2·4
OH 2 6 2·6 Me
OH Me 4 6 4·6
OMe Di Me
OH PrB I Me 4
OH PrB Me 2 4 2·4
OH PrB 2 Me CHO
OH PrB Me 4 6 4·6
OH PrB Me 6 CHO
OH 2 2·6 R*
OH MeO Mono 2·4
C3H5** Mono O Mono O–CH2
C3H5** Mono OMe Mono OMe
OH Mono OH Di
OH NO2 OH 4
OMe 4·6 OMe
OH CH2OH 4·6
OH NO2 6 CH2OH
OH 2·4
OH 2 SO3Na
OH 1 NaO3S OH 1

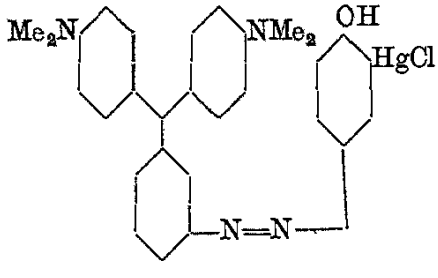
* R=tert-butyl or isoamyl. ** These compounds give two series of isomeric salts.

Derivatives of Phenol.

o-Chloromercuri phenol, $HO.C_6H_4.HgCl$.[1]—When an aqueous solution of mercuric acetate and phenol reacts at room temperature or by heating on the water-bath, three mercury compounds are obtained, two containing acetoxymercuri groups in the ortho- and para-positions to the hydroxyl group, and the third being a diacetoxymercuri derivative. The following method, due to Whitmore and Middleton, produces no dimercurated product, owing to the fact that no solvent is used. Phenol (12 grams) is heated on a steam-bath, and 25 grams of mercuric acetate gradually added, the mixture being well stirred. When the solution of the acetate is complete, boiling water is added, and the whole boiled for a few minutes, after which a hot solution of 5 grams of sodium chloride is poured in. The p-chloromercuri phenol is at once precipitated and filtered off, the filtrate on cooling depositing crystals of the ortho compound. This product can be further purified by crystallisation from hot water, when glittering crystals, M.pt. 152·5° C., are deposited. It forms an *acetyl* derivative, M.pt. 170° to 171° C., which does not react with potassium iodide, but if heated with concentrated hydrochloric acid and hydrogen sulphide, mercuric sulphide is formed. The acetyl compound is reduced to *mercuri-bis-o-phenol diacetate* when acted upon by sodium thiosulphate, a yield of 80 per cent. being obtained.

When o-chloromercuri phenol in sodium hydroxide solution is treated with sodium nitrite, the mixture cooled to —4° to —5° C., and acidified with concentrated sulphuric acid, *p-nitroso-o-chloromercuriphenol* is formed, $HO.C_6H_3.NO(4)HgCl(2)$. This substance crystallises from xylene or anisole in light brown needles, which respond to Liebermann's nitroso reaction and partially dissolve in ether, giving an intense green solution. Two grams of the nitroso compound, 2·4 grams of ammonium chloride, 6·6 grams of dry ammonium acetate, and 0·2 gram of ammonium carbonate when heated on the water-bath for thirty minutes with vigorous stirring yield *p-nitroso-o-chloromercuri aniline,* $NH_2.C_6H_3.NO(4).HgCl(2)$. The melt is poured into 75 c.c. of cold water and allowed to stand thirty minutes, when a brown amorphous precipitate settles out. This is filtered, well washed, dried, and crystallised from anisole. Its solutions in benzene and ether are green, in alcohol reddish-yellow.

When 2·43 grams of o-chloromercuri phenol in a freezing mixture are treated with the diazotised solution from 7 grams of m-amino-leuco-malachite green in 50 c.c. of water and 6 grams of hydrochloric acid (density 1·18) a dark green precipitate is obtained, which is brown-black when dry. It is *tetramethyldiaminotriphenylmethane-azo-o-chloro-mercuri phenol* and has the following constitution :—[2]



[1] Dimroth, *Ber.*, 1902, 35, 2853 ; Whitmore and Middleton, *J. Amer. Chem. Soc.*, 1921, 43, 619.

[2] Reitzenstein and Bönitsch, *J. prakt. Chem.*, 1912, [2], 86, 73.

o-Acetoxymercuri phenol.[1]—This product is obtained by a similar method to Whitmore and Middleton's o-chloromercuri phenol, *i.e.* using no solvent in the reaction. The compound crystallises in long needles or white, hexagonal, or rhombic prisms, M.pt. 157° C., decomposing at 210° to 215° C. In the usual way the following derivatives may be prepared: *hydroxide*; *internal oxide*; *bromide*, slender, silky needles, M.pt. 130° to 132° C., the liquid becoming turbid at 190° C. and decomposing at 195° C.; *iodide*, stellar aggregates of microscopic prisms, M.pt. 121° C., the clear red liquid becoming turbid at 170° to 180° C., and decomposing at 200° to 210° C.; *nitrate*, infusible compound, blackening about 200° C.; the *sulphate* and *hydroxide* are white, infusible powders.

p-Acetoxymercuri phenol crystallises in slender needles or triangular prisms, M.pt. 165° C., decomposing at 210° to 215° C.; the *bromide* forms scales, M.pt. 144° to 146° C., decomposing at 200° to 210° C.; the *iodide*, a white powder, M.pt. 134° to 135° C., decomposing at 200° to 210° C.; the *nitrate*, white crystals, decomposing at 210° C.; the *sulphate* and *hydroxide* are white, infusible compounds.

Diacetoxymercuri phenol.[2]—Phenol in concentrated aqueous solution is treated with mercuric acetate, when a white precipitate separates out, the reaction being accelerated if heat is applied. This product crystallises from dilute acetic acid in needles, M.pt. 216° to 217° C. The mother-liquor from this preparation contains o- and p-acetoxymercuri phenols.. Treatment of the diacetoxy compound with sodium chloride gives the *dichloromercuri phenol*, a white powder, M.pt. 258° C. with decomposition.[3]

p-Chloromercuri phenol.[4]—The preparation of this mercury compound has already been dealt with above. It crystallises from acetone or alcohol in needles, M.pt. 219° to 220° C. or 224° to 225° C., both figures being given in the literature. The sodium hydroxide solution when treated with alcohol yields the *sodium salt*, which on boiling with alcoholic methyl iodide yields *p-anisylmercuric chloride*. Boiling with hydrochloric acid gives mercuric chloride and phenol, and ethereal iodine solution gives mercuric iodide and p-iodophenol. The *acetyl* derivative melts at 235° C., and with sodium thiosulphate a 50 per cent. yield of mercuri-bis-p-phenol diacetate results.

Mercuri-bis-o-phenol, $HO.C_6H_4.Hg.C_6H_4.OH$.—o-Chloromercuri phenol dissolves in sodium thiosulphate solution, giving a clear solution which rapidly becomes cloudy, a white precipitate eventually separating out. In small quantities it may be recrystallised from alcohol, if the operation be conducted rapidly, small, white, glistening tablets being obtained. It is easily soluble in ethyl acetate or acetone, insoluble in water, benzene, ether, or chloroform. When heated alone its colour changes to gray without melting, but the alcoholic solution when rapidly boiled soon decomposes, metallic mercury separating out. It has the characteristic properties of a phenol, being soluble in caustic alkali,

[1] Mameli, *Gazzetta*, 1922, 52, i. 352.
[2] Dimroth, *Ber.*, 1898, 31, 2154; 1902, 35, 2853.
[3] See Mameli and Cocconi, *Gazzetta*, 1922, 52, ii. 113.
[4] Desesquelle, *Bull. Soc. chim.*, 1894, (3), 11, 268; Dimroth, *Ber.*, 1898, 31, 2155; 1899, 32, 761; Grützner, *Arch. Pharm.*, 1899, 236, 622; Whitmore and Middleton, *J. Amer. Chem. Soc.*, 1921, 43, 619.

insoluble in sodium carbonate, and is precipitated unchanged from its alkaline solutions by carbon dioxide.[1]

Derivatives of Anisole.[2]

Mercuri-bis-o-anisole.—The best method of obtaining this compound is that due to Whitmore and Middleton, which consists of heating o-iodomercuri anisole with alcoholic potassium iodide solution in a reflux apparatus. It also occurs as a by-product in the preparation of o-iodomercurianisole, from which compound it may also be derived by the action of sodium stannite solution.

The usual method for preparation of compounds of the type R_2Hg is also available, namely, heating together o-bromoanisole and 1·5 per cent. sodium amalgam.

It crystallises from hot alcohol in prisms, M.pt. 108° C., soluble in chloroform and benzene. When treated with mercuric chloride in alcoholic solution it yields the chloride, and when dissolved in hot acetic acid, *o-acetoxymercuri-anisole* (M.pt. 123° to 124° C.) is formed, which may be precipitated by the addition of water.

o-Chloromercuri anisole.—This was first obtained in small yield by Dimroth, when dry mercuric acetate was warmed with excess of anisole. After removal of the p-acetoxymercuri anisole, the mother-liquors are treated with sodium chloride, and the mixture steam distilled, the excess of anisole passing over; the product is recrystallised from benzene, and has M.pt. 173° to 174° C. It crystallises from alcohol in needles and from chloroform in plates. When obtained by heating mercuri-bis-o-anisole (1 gram) with 0·7 gram of mercuric chloride in 25 c.c. of alcohol for fifteen minutes, the crystals melt at 177° to 178° C. The corresponding *bromide* melts at 183° C.

o-Iodomercuri anisole is best prepared by gently heating an alcoholic alkaline solution of o-chloromercuri phenol with methyl iodide; it is also formed when the chloride is treated with potassium iodide solution. It crystallises in colourless needles, M.pt. 165° C., which react with alcoholic potassium iodide to form mercuri-bis-o-anisole.

Mercuri-bis-p-anisole.[3]—p-Bromoanisole (100 grams), 80 grams of xylene, 1/10 the volume of ethyl acetate, and sufficient 1·5 per cent. amalgam to give double the quantity of sodium required in the reaction are heated in an oil-bath at 160° C. for twenty-four hours. The flask should be frequently shaken, and more ethyl acetate added at eight-hour intervals. The residue obtained crystallises from hot benzene in transparent needles, 200 grams of p-bromoanisole yielding about 80 grams of pure product. It melts at 202° C., sublimes on strong heating, and is readily soluble in hot benzene or cold chloroform. Prolonged heating with hydrochloric acid decomposes it to anisole and mercuric chloride. It readily reacts with phosphorus and bismuth chlorides, forming mercuric chloride and phosphorus or bismuth anisyl halides.

[1] For mercury compounds of p-chlorophenol, see German Patent, 234851; phenol and cresol sulphonic acids, German Patent, 410969; phenol-p-sulphonic acid, Rupp and Herrmann, *Arch. Pharm.*, 1916, 254, 500.

[2] Dimroth, *Ber.*, 1902, 35, 2853; Manchot, *Annalen*, 1920, 421, 340; Whitmore and Middleton, *J. Amer. Chem. Soc.*, 1923, 45, 1753; Michaelis, *Ber.*, 1894, 27, 257.

[3] Michaelis and Rabinerson, *Ber.*, 1890, 23, 2342.

p-Chloromercuri anisole may be obtained :

1. By mixing alcoholic solutions of mercuric chloride and mercury dianisyl.

2. By boiling the alcoholic solution of the double salt of trianisyl stibine and mercuric chloride, $(OMe.C_6H_4)_3Sb.HgCl_2$.[1]

3. By adding sodium chloride to the product obtained when 1 mol. of anisole and 1 mol. of mercuric acetate react in aqueous solution.[2]

It crystallises in colourless, pearly plates, M.pt. 239° C., readily soluble in hot benzene or cold chloroform, but with difficulty in alcohol. With arsenic trichloride on heating it forms anisyl dichloroarsine.[3]

The *bromide* is a similar compound, M.pt. 187° C. ; the *iodide* forms colourless plates, M.pt. 227° C., and may be prepared by the use of potassium iodide, or by heating p-hydroxymercuri phenol with methyl iodide in alkaline alcoholic solution.

The compound mentioned in method 3 above, obtainable from mercuric acetate and anisole, is stated by Manchot to possess the formula :

$$(C_7H_8O.HgOH)OH \quad \text{or} \quad C_7H_8O.Hg(OH)_2$$

It crystallises in white needles, sintering at 164° C. and melting at 169° C. Another method of preparation is as follows: 7·8 grams of anisole (1 mol.) and 70 grams (3 mols.) of mercuric acetate in 700 c.c. of water are maintained at 50° C. and shaken for half-hour periods during three to four days. The product when crystallised from 25 per cent. acetic acid is obtained in fine needles, M.pt. 173° C., and although its melting-point differs from that of the first preparation, analysis shows the two compounds to be identical. The substance is unchanged when treated with sodium hydroxide, ammonium hydroxide, or sulphide, but decomposes when warmed with dilute hydrochloric acid. The above formulæ have recently been criticised by Dimroth,[4] who has shown that Manchot's compound consists of a mixture of p-acetoxymercuri anisole and **2 : 4-diacetoxymercuri anisole**, M.pt. 197° C.

p-Acetoxymercuri anisole. $MeO.C_6H_4.HgOAc$.—Dry mercuric acetate and excess of anisole (8 mols.) are heated on the water-bath until a test portion gives no precipitate with sodium hydroxide. The solution on cooling deposits crystals of the acetate, which crystallise from dilute alcohol in needles, M.pt. 176·5° C. The mother-liquors from this preparation contain o-acetoxymercuri anisole.

A similar product is obtained when mercuri-bis-p-anisole is dissolved in acetic acid. The substance yields the chloride when treated with aqueous sodium chloride.

p-Anisylmercuric oxide,

$$O\begin{matrix}\diagup Hg.C_6H_4.OMe \\ \diagdown Hg.C_6H_4.OMe\end{matrix}$$

When the preceding halogen compounds are treated with aqueous sodium carbonate, the oxide is deposited as the solution cools. It crystallises from alcohol in fine, white needles, M.pt. 177° C., easily soluble in alcohol or hot sodium carbonate, but with difficulty in water.

[1] Löloff, *Ber.*, 1897, 30, 2836.
[2] Manchot, *Annalen*, 1920, 421, 340.
[3] Roeder and Blaise, *Ber.*, 1914, 47, 2752.
[4] Dimroth, *Ber.*, 1921, 54, [B], 1504.

The solution has an alkaline reaction and absorbs carbon dioxide from the air.

Derivatives of p-Allyl anisole, Methyl chavicol.[1]—When treated with mercuric acetate this compound yields a syrup, from which two *chlorides* and *bromides* are obtainable. The first chloride is soluble in alcohol but insoluble in water, and forms white, glistening needles, M.pt. 81° to 82° C.; the isomeride forms a resinous mass, insoluble in alcohol. The second chloride hardens when first heated, but softens at 55° C. without showing any definite melting-point, and both isomers yield p-allyl anisole on reduction. The *acetate* gives a *bromide*, white needles, M.pt. 70° C., and also a resinous isomeride.

Derivatives of Phenetole.

Mercuri-bis-o-phenetole is obtained:

1. By heating o-iodomercuri phenetole under reflux with alcoholic potassium iodide, thiocyanate, or sodium thiosulphate.[2]

2. As a by-product in the preparation of o-iodomercuri phenetole (see below).

3. From o-bromophenetole and sodium amalgam.[3]

The substance crystallises in needles, M.pt. 83° C., is soluble in the usual organic solvents, and has similar properties to the anisyl derivative.

The following compounds have been obtained from it in the usual manner: *o-acetoxymercuri phenetole*, tablets, M.pt. 150° to 155° C.; *chloride*, needles, M.pt. 132° C.; *bromide*, needles or prisms, M.pt. 121° C.; *iodide*, needles or prisms, M.pt. 111·5° C. Whitmore's preparation of the latter compound is of interest. Five grams of o-chloromercuri phenol in 50 c.c. of 50 per cent. alcohol, 0·7 gram of sodium hydroxide, and 3·5 grams of ethyl iodide are gently heated on the water-bath for one hour. On cooling a small quantity of mercuri-bis-o-phenetole separates out and is removed. Addition of water precipitates the iodide. Yield 7 grams.

Mercuri-bis-p-phenetole separates as leaflets from benzene, M.pt. 135° C. It is obtained by the amalgam method.

p-Acetoxymercuri phenetole occurs as tablets, sintering at 100° C. and melting at 162° C. It is prepared by the same methods as used for the anisyl compound.

p-Chloromercuri phenetole.—The melting-point of this compound appears to differ slightly according to the method of preparation. From the acetate by aqueous sodium chloride, the M.pt. is 234° C.;[4] from mercuri-bis-p-phenetole and mercuric chloride, M.pt. 241·5° C.;[5] from the compound $EtO.C_6H_5.Hg(OH)_2$, and sodium chloride, M.pt. 238° C.[6] It may also be prepared by boiling an alcoholic solution of $(C_8HgO)_3Sb.HgCl_2$. The *bromide* crystallises in needles or leaflets, M.pt. 241·5° C., and the *iodide* in needles, M.pt. 216° C. The *oxide* is deposited in fine needles from alcohol, M.pt. 202° C.

The *compound*, $EtO.C_6H_5.Hg(OH)_2$ or $(EtO.C_6H_5.HgOH)OH$, is pre-

[1] Balbiano and Paolini, *Ber.*, 1903, 36, 3580; *Gazzetta*, 1906, 36, 1. 264; Balbiano, *Ber.*, 1909, 42, 1505.

[2] Whitmore and Middleton, *J. Amer. Chem. Soc.*, 1923, 45, 1753.

[3] Michaelis, *Ber.*, 1894, 27, 261; Dimroth, *ibid.*, 1899, 32, 758.

[4] Dimroth, *loc. cit.*; Michaelis, *Ber.*, 1894, 27, 259.

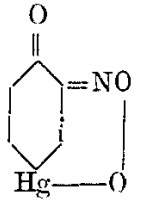
[5] Michaelis, *loc. cit.*

[6] Manchot, *Annalen*, 1920, 421, 340.

pared as follows : 12·2 grams of phenetole (1 mol.) and 31·8 grams of mercuric acetate in 318 c.c. of water are heated at 50° C. for ten days, with frequent shaking. Yield 18 grams. It crystallises from dilute alcohol in small needles, M.pt. 135·5° C., from methyl alcohol in spherical or globular aggregates, from water in fine silky needles. When warmed with dilute hydrochloric acid it decomposes, but with 10 per cent. potassium bromide, a *bromide*, M.pt. 193° C., is isolated, which is probably an impure form of the bromide referred to above, M.pt. 241·5° C. It has been stated more recently [1] that the compound, $EtO.C_6H_5.HgOH$, can be separated into p-acetoxymercuri phenetole and **2 : 4-diacetoxymercuri phenetole**, M.pt. 183° to 184° C.

Derivatives of Nitrophenols.

Anhydride of 4-hydroxymercuri-2-aci-nitrophenol,[2]



The sodium salt of o-nitrophenol is shaken with the calculated amount of mercuric acetate in aqueous solution, when the anhydride separates out as a yellow precipitate. When treated with bromine or iodine in potassium iodide, bromo-2-nitrophenol and iodo-2-nitrophenol result.

4-Chloromercuri-2-nitrophenol is formed when the above anhydride is treated with hydrochloric acid. It forms colourless solutions in acetic acid or acetone, but yellow solutions in pyridine ; it is somewhat soluble in alcohol or ether and insoluble in chloroform.

4-Hydroxymercuri-2-nitrophenol forms pale yellow crystals, M.pt. 240° to 250° C., obtained by treating a sodium hydroxide solution of the anhydride with dilute sulphuric acid. It is readily soluble in acetone, less soluble in hot alcohol, and insoluble in water. Its *sodium salt* crystallises from alcohol in dark red crystals.

4-Acetoxymercuri-2-nitrophenol.[3]—To a warm solution of 10 grams of o-nitrophenol in 200 c.c. of water and 10 c.c. of 40 per cent. sodium hydroxide, a solution of 22·3 grams of mercuric acetate in 200 c.c. of water plus a few drops of acetic acid is added drop by drop. The precipitate first formed is orange, but after two hours' stirring this becomes pale yellow, when it is filtered and washed with very dilute boiling acetic acid. The product obtained is dissolved in 5 per cent. sodium hydroxide, filtered and re-precipitated by acetic acid, the resulting substance after washing and drying weighing about 16 grams. It is easily soluble in hot glacial acetic acid, but insoluble in ordinary organic solvents.[4]

6-Acetoxymercuri-2-nitrophenol.—A mixture of 15 grams of o-nitrophenol and 3 grams of mercuric acetate is gradually heated to 150°

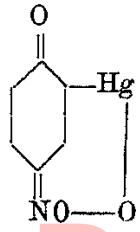
[1] Dimroth, *Ber.*, 1921, 54, [B], 1504.
[2] Hantzsch and Auld, *Ber.*, 1906, 39, 1105.
[3] Raiziss and Proskouriakoff, *J. Amer. Chem. Soc.*, 1922, 44, 787; see Hodgson, *ibid.*, 1927, 49, 2840.
[4] Hodgson, *loc. cit.*

C. during one hour, then kept at 140° to 150° C. with frequent shaking for four hours. The reaction mixture is then treated with a saturated solution of sodium chloride and steam distilled. From the non-volatile residue 2 grams of 6-*chloromercuri*-2-*nitrophenol* is obtained by extraction with boiling alcohol. The light brown colourless residue is dissolved in dilute sodium hydroxide, filtered and re-precipitated by acetic acid. Crystallisation from acetic acid gives a pale brownish-yellow product, unmelted below 300° C. The product is transformed by iodine in potassium iodide to 6-iodo-2-nitrophenol.

The melting-points and crystalline forms of the 6- and 4-halide-mercuri-2-nitrophenols is as follows: 6-*fluoro*-, pale yellow plates, M.pt. 187° C.; 6-*chloro*-, pale yellowish-brown rectangular plates, M.pt. 185° C.; 6-*bromo*-, pale yellow plates, M.pt. 177° C.; 6-*iodo*-, deep yellow needles, M.pt. 215° C.; 4-*fluoro*-, micro-crystalline plates, M.pt. 195° C.; 4-*chloro*-, creamy yellow micro clusters, M.pt. 205° C.; 4-*bromo*-, needles, M.pt. 236° C.; 4-*iodo*-, bright yellow needles, M.pt. above 300° C.

Sodium - 6 - hydroxymercuri - 2 - nitrophenolate gives scarlet crystals; the 4-compound is deeper red.[1]

Anhydride of 2-hydroxymercuri-4-aci-nitrophenol,[2]



This product is a yellow powder, formed by prolonged boiling of a dilute alcoholic solution of mercuric acetate with sodium p-nitrophenoxide. It yields a *double salt* with pyridine, which is a scarlet powder decomposing at 190° C. into its constituents. The mercury must be ortho to the hydroxyl group, since 2 : 6-dibromo-p-nitrophenol does not yield a corresponding derivative. The anhydride does not react with potassium iodide or hydrogen sulphide, but with iodine it gives mercuric iodide and o-iodo-p-nitrophenol.

2-Chloromercuri-4-nitrophenol occurs as colourless crystals, M.pt. 175° C. It may be obtained by adding hydrochloric acid to the anhydride, or by treating the mixture used in the preparation of the acetoxymercuri compound with warm dilute sodium hydroxide, when an orange deposit of the monosodium salt appears on cooling. This is filtered off, dissolved in water, and the solution acidified with hydrochloric acid, when the chloride is deposited as a white precipitate, which is recrystallised from 50 per cent. alcohol. The chloride is soluble in alcohol and ethyl acetate.

2-Hydroxymercuri-4-nitrophenol, obtained from the sodium salt, is an amorphous powder, M.pt. 206° C., soluble in acetone, alcohol, or acetic acid, giving colourless solutions, but a slightly yellow solution in pyridine. Its *sodium* salt contains 0·5 mol. of water of crystallisation, is easily soluble in water, and darkens when heated.

2-Acetoxymercuri-4-nitrophenol.—Aqueous solutions of equi-

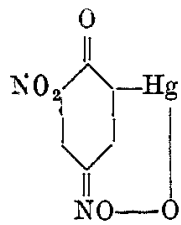
[1] For compounds from o-nitrophenol with mercuric nitrate and 4-chloro-2-nitrophenol with mercuric oxide, see German Patent, 234851.

[2] Raiziss and Proskouriakoff, *loc. cit.*

molecular quantities of mercuric acetate and sodium p-nitrophenolate are boiled for two hours, the yellow precipitate washed with water and recrystallised from hot glacial acetic acid. This compound is dried for three days over calcium chloride and found to contain some dimercurated derivative when analysed.[1]

2 : 2′-Mercuri-bis-4-nitrophenol[2] is isolated from its sodium salt, the latter being obtained from the corresponding oxide by reduction with sodium sulphide. This oxide is formed from sodium p-nitrophenolate and mercuric acetate, the two being boiled in aqueous solution.

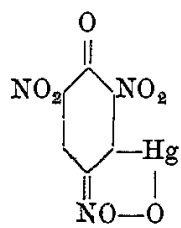
Anhydride of 2-Hydroxymercuri-4-aci-nitro-6-nitrophenol,[3]



Freshly precipitated mercuric oxide and the calculated quantity of dinitrophenol are boiled together in aqueous solution for sixteen hours, a lemon-yellow powder resulting which is only slightly soluble in water or alcohol, and insoluble in other solvents except pyridine. When heated with the latter it forms a *double compound* which may be precipitated by the addition of ether. This derivative is dark yellow in colour and is decomposed when heated, and in aqueous solution it yields no mercury ions. When the anhydride is treated with bromine, o-bromodinitrophenol is formed, and with dilute hydrochloric acid the *chloromercuri* derivative is obtained, a colourless, crystalline powder, M.pt. 182° C. with decomposition.

2-Hydroxymercuri-4 : 6-dinitrophenol, obtained as a microcrystalline powder from alcohol, is neutral to litmus. It may be prepared from its *sodium salt*. The latter is formed when the chloride is treated with concentrated sodium hydroxide, and it crystallises from water or alcohol in orange-red prisms containing 1 mol. of water of crystallisation, and which explode when strongly heated.

Anhydride of 3-hydroxymercuri-4-aci-nitro-2 : 6-dinitrophenol,



Mercuric oxide (8·4 grams) is shaken for several hours with a solution of 15 grams of picric acid in 800 c.c. of water at 80° C., when orange-yellow needles separate. If this mixture is then boiled the anhydride results. It yields small, pale yellow crystals which are only slightly soluble in the usual solvents and decompose without melting. In aqueous solution it is a non-electrolyte, and with dilute hydrochloric acid the *chloro-*

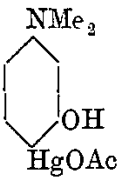
[1] Raiziss and Proskouriakoff, *J. Amer. Chem. Soc.*, 1922, 44, 787.
[2] Fourneau and Vila, *J. Pharm. Chim.*, 1912, [vii.], 6, 433.
[3] Hantzsch and Auld, *Ber.*, 1906, 39, 1105.

mercuri compound is formed, pale yellow crystals, M.pt. 118° C. These crystals with sodium hydroxide give the *sodium salt*, yellow needles, which in turn are decomposed by dilute sulphuric acid, yielding the *hydroxymercuri* derivative.

Derivatives of Aminophenols.

2 : 2′-Mercuri-bis-4-aminophenol[1] is obtained from the corresponding nitro compound by reduction in alkaline solution with sodium hydrosulphite. It forms heavy needles, insoluble in water, but readily soluble in alcohol. The *hydrochloride* crystallises in brilliant needles, soluble in water. The *free base* in alkaline solution is rapidly oxidised on exposure to air, and its *acetyl* derivative crystallises in slender needles, soluble in alkali, forming stable solutions.

4-Acetoxymercuri-m-dimethylaminophenol[2]



A solution of 2·8 grams of m-dimethylaminophenol in 10 c.c. of alcohol is mixed with 7 grams of 90 per cent. mercuric acetate in 30 c.c. of water. A jelly forms, and this when heated for two minutes on the water-bath melts, and yellow crystals separate. The precipitate is collected, washed with water, and dried *in vacuo*. Yield 7·4 grams, 92 per cent. It forms dirty yellow crystals, insoluble in the usual solvents, except pyridine. It dissolves in sodium hydroxide, and the solution may be boiled without decomposition. In water it only dissolves to a slight extent, the solution giving mercuric sulphide on addition of ammonium sulphide. When the dry product stands for two weeks metallic mercury separates out. If the substance is slowly heated it melts with decomposition at 100° to 110° C.

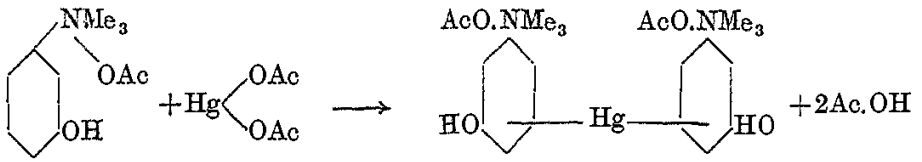
When m-dimethylaminophenol is heated with mercuric acetate in equimolecular proportions mercury is precipitated, and a mercury-free pink dye is formed.

The acetoxymercuri compound when methylated yields *4-acetoxymercuri-m-dimethylaminoanisole hydrochloride*, pink leaflets, M.pt. 140° to 150° C., and at 190° C. it decomposes with evolution of gas and formation of a pink, fluorescent dye.

4-Acetoxymercuri-m-dimethylaminophenyl acetate is prepared as above, using m-dimethylaminophenyl acetate. Yield 78 per cent. It forms colourless crystals, M.pt. 110° C. (corr.), readily soluble in hot alcohol. The cold alcoholic solution with ammonium sulphide gives a yellow precipitate which blackens in a few minutes. When the substance is warmed for a few minutes with dilute sodium hydroxide, cooled and neutralised with acetic acid, ammonium sulphide immediately gives mercuric sulphide. This is no doubt due to the hydrolysis of the acetyl group by alkali and the formation of the less stable mercury derivative of m-dimethylaminophenol. The dry acetate blackens when kept for several months.

[1] Fourneau and Vila, *J. Pharm. Chim.*, 1912, [vii.], 6, 433.
[2] Kharasch and Chalkley, *J. Amer. Chem. Soc.*, 1924, 46, 1211.

Mercuri-bis-m-hydroxyphenyl-trimethylammonium acetate.—A solution of 5·6 grams of m-hydroxyphenyl-trimethylammonium iodide in 20 c.c. of water is shaken with the silver oxide from 4·6 grams of silver nitrate. After ten minutes the solution is filtered and neutralised with acetic acid. It is mixed with a solution of 7·1 grams of 90 per cent. mercuric acetate, and the mixture heated until a test portion gives a yellow and not a black precipitate with ammonium sulphide. The solution is evaporated to dryness *in vacuo* and the residue dissolved in about 15 c.c. of alcohol, and 275 c.c. of acetone added. The solution is warmed until clear, then the liquor poured off, 450 c.c. of acetone added, and the whole allowed to stand for twenty-four hours, when colourless crystals separate. These are collected and dried *in vacuo*. Yield 2·2 to 2·8 grams, 53 to 69 per cent., calculated on the following equation :—



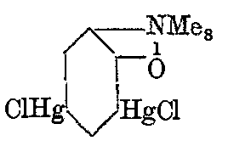
It may be purified by solution in alcohol and precipitation with acetone. The substance is a white, very hygroscopic powder, which melts with decomposition and evolution of gas at 116° to 117° C. (corr.). It is soluble in water or alcohol, but insoluble in ether. Its aqueous solutions decompose on standing for a week, yielding a white precipitate and inorganic mercury in solution.

3-Chloromercuri-m-hydroxyphenyl-trimethylammonium anhydride.—A solution of 2·3 grams (1 mol. equivalent) of the preceding compound in 5 c.c. of 60 per cent. alcohol is treated with 0·9 gram (0·9 molecular equivalent) of mercuric chloride in 12 c.c. of 60 per cent. alcohol. The suspension is shaken and gently warmed until practically all the precipitate has dissolved, the liquor poured off and allowed to stand for twenty-four hours. From this, 0·6 gram of solid is obtained, 25 per cent. The dry compound is insoluble in cold water, but readily dissolves in dilute acetic acid. It melts with decomposition at about 130° to 150° C., turning purple.

2 : 6-Diacetoxymercuri-p-hydroxyphenyl-trimethylammonium acetate, $C_6H_2(1)OH(4)NMe_3.OCOCH_3(2:6)(HgOAc)_2$, forms large colourless needles which, when slowly heated, decompose with gas evolution at about 155° to 160° C. It is extremely soluble in water, insoluble in benzene, acetone, or ether.

2-Chloromercuri-p-hydroxyphenyl-trimethylammonium acetate, $C_6H_3(1)OH(4)NMe_3.OCOCH_3(2)HgCl$, obtained from the mother-liquors of the preceding compound, decomposes at 155° to 160° C., turning blue-green. It is soluble in pyridine, sparingly in water, and is stable when dry.

3 : 5-Dichloromercuri-o-hydroxyphenyl-trimethylammonium anhydride,



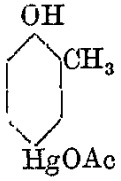
The product of reaction between o-hydroxyphenyltrimethylammonium

hydroxide and mercuric acetate is treated with sodium chloride. The compound is practically insoluble in water, but dissolves in dilute sodium hydroxide, acetic acid, or pyridine. When heated it suddenly becomes violet at about 200° to 210° C., and 5° or 10° higher suddenly becomes brick-red and decomposes.

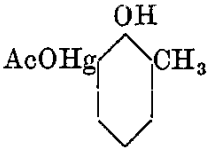
(4 : 6)? **Dichloromercuri - m - aminophenyl - trimethylammonium acetate** is obtained by the action of mercuric acetate on m-aminophenyl-trimethylammonium chloride. It forms colourless or pale brown crystals which decompose at 200° C. It is sparingly soluble in water, the solution giving an immediate black precipitate with ammonium sulphide.[1]

Derivatives of Cresols.

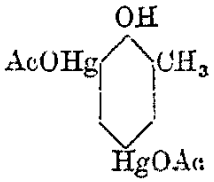
The mercuration of o-cresol by mercuric acetate in aqueous acetic acid solution, using equimolecular quantities of the reagents, gives rise to three products, in yields as given below : [2]

I. 

50·3 to 62·3 per cent.

II. 

13·4 to 20·7 per cent.

III. 

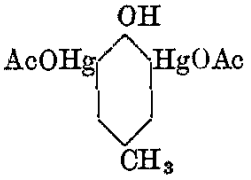
2·6 to 7·0 per cent.

4-Acetoxymercuri-o-cresol (I.) melts at 153° to 155° C. and decomposes at 186° to 190° C.; it is converted by bromine into 4-bromo-o-cresol, and yields a *chloromercuri* compound, melting with decomposition at 200° to 202° C., and a *nitratomercuri* derivative, M.pt. 212° to 213° C. with decomposition.

6-Acetoxymercuri-o-cresol (II.) melts at 123° to 125° C. and decomposes at 191° C., and is transformed into 6-bromo-o-cresol on bromination. Its *chloride* and *nitrate* melt at 160° to 162° C. and 208° to 210° C. respectively with decomposition.

4 : 6-Diacetoxymercuri-o-cresol (III.).—The yield of the product may be increased by raising the temperature in the above reaction or by using 2 mols. of mercuric acetate. The diacetoxy compound melts with decomposition at 192° to 195° C., and yields *dichloromercuri* and *dinitratomercuri* derivatives, melting with decomposition at 210° to 212° C. and 222° C. respectively. The above three compounds when nitrated give 4 : 6-dinitro-o-cresol.

2 : 6-Diacetoxymercuri-p-cresol,[3]



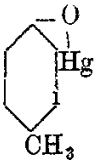
When p-cresol is mercurated, using mercuric acetate, two products are formed, one a monoacetoxymercuri and the other a diacetoxymercuri

[1] For mechanism of mercuration of o-acetaminophenols, see Maschmann, *Annalen*, 1926, 450, 85.
[2] Mamelli, *Gazzetta*, 1926, 56, 948.
[3] Dimroth. *B r.*, 1902, 35, 2853.

compound. To 21·6 grams of mercuric oxide in 500 c.c. of water, 10·8 grams of p-cresol in a little alcohol and 18 grams of acetic acid are added. If left at room temperature the reaction is complete in two days, but if carried out at 90° C. it only takes thirty minutes. The mixture is filtered whilst hot, and the residue is almost pure diacetoxymercuri compound. It crystallises from dilute acetic acid in granular crystals, which contain 1 mol. of water of crystallisation when dried in air, and when heated it decomposes at about 200° C. without melting.

Chloromercuri-p-cresol is obtained from the warm mother-liquors in the above preparation by the addition of sodium chloride. It separates in fine needles, which are contaminated with the chloride from the diacetoxy compound. To effect a separation the mixture is treated with cold alcohol, the solvent partially removed, and the substance precipitated by water and recrystallised from hot benzene, when long branching needles are obtained. These are readily soluble in cold alcohol and melt at 166° C. to a clear liquid, which at 176° C. becomes turbid, and again solidifies at 183° C. Its *benzoyl* derivative melts at 241° to 242° C. The corresponding *iodide* cannot be obtained by the addition of potassium iodide to the acetate, since this precipitates mercuric iodide; but when the chloride is treated with a large bulk of boiling water and potassium iodide is added, the iodide separates out in fine needles. These become yellow at 145° C. and red at 170° C., partial decomposition taking place and the substance subliming. It is easily soluble in ether or alcohol, with difficulty in benzene or chloroform, but prolonged boiling with alcohol or benzene tends to decompose it, although it is quite stable in boiling water. When treated with iodine it forms mercuric iodide and o-iodo-p-cresol.

Anhydride of o-hydroxymercuri-p-cresol,



1. The chloride is dissolved in dilute sodium hydroxide and carbon dioxide passed in, the anhydride being precipitated.

2. By adding the requisite amount of boiling sodium carbonate solution to an alcoholic solution of the chloride.

It is a fine white powder, insoluble in the usual solvents, but soluble in phenol. When dissolved in an excess of 12 per cent. sodium hydroxide, carbon dioxide passed in, and the mixture slowly cooled, the *sodium salt* separates in needles which are decomposed when exposed to light. Treatment of the anhydride with hot dilute acetic acid gives the *o-acetoxymercuri* compound, which sinters at 150° C. and melts with decomposition at 163° C.

Mercuration of p-cresol methyl ether.[1]—The ether (4·8 grams; 1 mol.) is shaken with a solution of 38·4 grams of mercuric acetate (3 mols.) in a stoppered flask for several days at 50° C. The precipitate is then removed and washed with water until the washings give no reaction for mercury. About 12 grams of product are obtained which, after crystallisation from 20 per cent. acetic acid and then from alcohol, yield long needles, M.pt. 131·5° C. When the ether and mercuric salt are used in

[1] Manchot, *Annalen*, 1920, 421, 335.

the proportion 1 : 1, the resulting product melts at 132° C.[1] Analysis of this substance agrees with the formula :

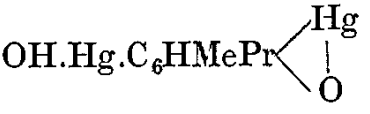
$$3Me.C_6H_4.OMe.Hg(C_2H_3O_2)_2.2HgO$$

It is unaffected by ammonium sulphide or sodium hydroxide, but when its clear alcoholic solution is treated with aqueous sodium chloride, *chloromercuri-p-cresol methyl ether*, $Me.C_6H_4.OMe.HgCl$, is precipitated. This crystallises from 96 per cent. alcohol in white needles, M.pt. 162° C., which are not acted upon by ammonium hydroxide, sulphide, or sodium hydroxide, although easily soluble in the latter.

Derivatives of Thymol.[2]

o(?)-Chloromercuri thymol.—To a hot alcoholic solution of 5 grams (1 mol.) of thymol, 10·6 grams (1 mol.) of mercuric acetate in acetic acid-alcohol solution are added, and the mixture boiled for one hour. On cooling, a slight precipitate of 0·5 gram of dimercuri compound is deposited, and after filtering, sodium chloride solution is added, when chloromercuri thymol is obtained as a voluminous precipitate. This is recrystallised from 40 per cent. alcohol, hair-fine needles, M.pt. 139·5° C., being deposited. Yield 10 grams. The substance is readily soluble in dilute sodium hydroxide, but if the latter is too concentrated the *sodium salt* is produced.

2 : 6-Diacetoxymercuri thymol is formed when 2 mols. of mercuric acetate are used to 1 mol. of thymol, the reaction being carried out in boiling alcoholic solution containing some acetic acid. After a time the mixture which practically solidifies is cooled, filtered, and recrystallised from ethyl acetate-acetic acid mixture, white shining needles coming down. These melt at 215° to 216° C. with decomposition, and are soluble in sodium hydroxide, from which the *sodium salt* crystallises in plates.[3] A hot 10 per cent. solution of sodium hydroxide yields 2 : 6-*dihydroxymercuri thymol*, which crystallises in colourless plates, containing 3 mols. of water of crystallisation; in aqueous solution it is converted by carbon dioxide into the *anhydride*,



With sodium chloride, 2·6-*dichloromercuri thymol* is formed. M.pt. 210° to 211° C. with decomposition, which may be reduced to thymol by zinc and potassium hydroxide. The corresponding *iodomercuri* compound is also known, and a 2 : 6-*dinitratomercuri thymol* formed from the diacetate and 5 per cent. nitric acid.

2-Acetoxymercuri thymol, prepared in the usual manner, forms a lustrous, white powder, M.pt. 147° C., decomposing at 182° C., and giving an immediate precipitate with ammonium sulphide, but with hydrogen sulphide only in the presence of hydrochloric acid. With sodium chloride the 2-*chloromercuri* derivative is formed, M.pt. 144° to 145° C., decomposing about 160° C.[4] This compound is probably

[1] Dimroth, *Ber.*, 1921, 54, [B], 1504, gives the melting-point as 136° C.
[2] Dimroth, *Ber.*, 1902, 35, 2853.
[3] See Merck, *Arch. Pharm.*, 1893, 231, 124; Paolini, *Gazzetta*, 1921. 51, ii. 188; Rupp, *Arch. Pharm.*, 1917, 255, 191.
[4] Mameli and Mameli-Mannessier, *Gazzetta*, 1922, 52, ii. 1.

identical with Dimroth's chloride mentioned above. The following thymol-2-derivatives are also known: *Bromide*, crystalline powder, contracting at 140° C. and reddening and subliming at 180° C.; *sulphate*, amorphous, white powder, reddening without melting at 220° C.; *nitrate*, pink powder, M.pt. 148° to 150° C., decomposing at 155° C. and turning violet in the light; *oxide*, white precipitate, M.pt. 195° C. with decomposition.

6-Acetoxymercuri thymol occurs as small, lustrous crystals, M.pt. 163° C., decomposing at 178° to 180° C. The *bromide* is a white compound, M.pt. 149° C. with decomposition; *sulphate*, amorphous powder, decomposing at 235° C.; *nitrate*, white powder, M.pt. 167° C. with decomposition; *oxide*, white powder, blackening at 180° C., and decomposing about 205° C.; *hydroxide*, M.pt. 190° to 195° C. with decomposition.

2-Acetoxymercuri-6-iodothymol[1] forms white crystals, reddening at 170° C. and melting at 175° C. with decomposition; the *chloride* turns yellow at 119° C. and melts at 122° to 124° C.; the *bromide* turns yellow at 102° C., M.pt. 105° to 108° C.; *oxide*, M.pt. 162° to 165° C. with decomposition.

3-Acetoxymercuri-4-hydroxy-2-methyl-5-isopropyl-benzaldehyde.[2]—Molecular proportions of 4-hydroxy-2-methyl-5-isopropylbenzaldehyde (p-thymolaldehyde) and mercuric acetate, in alcoholic solution containing a little acetic acid, are boiled for fifteen minutes and cooled. The precipitated product crystallises from acetone containing a small quantity of acetic acid in colourless, hard prisms, sintering at 179° C. and decomposing at 185° C. Iodine in potassium iodide solution splits off the mercury, with probable formation of 3-iodo-4-hydroxy-2-methyl-5-isopropylbenzaldehyde, pale yellow, octagonal prisms, M.pt. 128° to 129° C.

Derivatives of Carvacrol.[3]

Acetoxymercuri and Diacetoxymercuricarvacrol.—Solutions of carvacrol (1 mol.) and mercuric acetate (2 mols.) in 50 per cent. alcohol are boiled for fifteen minutes, then cooled, a crystalline substance separating out. Concentration of the filtrate gives a pale yellow oil, which may be crystallised on warming with alcohol. The mother-liquors from the oil are mixed with the alcoholic filtrate from the solid, and the above process of concentration, etc., repeated. In this way eight crops of crystals are obtained, the fourth and sixth being mercurous acetate, and 18 grams of carvacrol give 61·3 grams of crude mercury compound. The first two crops (34 grams) are practically pure monomercuri derivative, crops 3, 5, and 7 (21·8 grams) nearly pure diacetoxymercuri compound, whilst 8 consists of 5·5 grams of a mixture of the two compounds. One crystallisation of the above 34 grams gives pure acetoxymercuricarvacrol, in short, highly refractive, colourless crystals, decomposing at 196° C. Similarly crops 3, 5, and 7 yield the diacetoxymercuricarvacrol in colourless, well-formed prisms, sintering at 190° C. and decomposing at 215° C. Although orientation experiments are not very satisfactory in the case of three compounds, and since the mercuri residue apparently never enters the benzene ring in the meta

[1] Mameli, *Gazzetta*, 1922, 52, ii. 18.
[2] Henry and Sharp, *J. Chem. Soc.*, 1926, p. 2436.
[3] Henry and Sharp, *loc. cit.*

position to a hydroxyl group, these compounds are probably 4- or 6-monoacetoxymercuri and 4 : 6-diacetoxymercuricarvacrols (OH in position 1).

5 - Chloromercuri - 4 - hydroxy - 3 - methyl - 6 - isopropylbenzaldehyde.—Molecular proportions of 4-hydroxy-3-methyl-6-isopropylbenzaldehyde (p-carvacrolaldehyde) and mercuric acetate in alcohol containing acetic acid are boiled for 1·25 hours. The solution is filtered and treated with an excess of 10 per cent. aqueous sodium chloride, when a pale cream-coloured precipitate is thrown down. This is filtered off, dried, and recrystallised from acetone containing one drop of hydrochloric acid, small, four-sided plates being deposited, which sinter and darken about 209° C. and decompose indefinitely about 260° C. A 50 per cent. yield of the corresponding *5-acetoxymercuri* derivative is obtained when molecular proportions of p-carvacrolaldehyde and mercuric acetate are heated for 1·5 hours on the water-bath. A yellow oil is formed, and this after extraction with hot ligroin is dissolved in a little acetic acid and the solution filtered. On cooling, colourless needles of 4-hydroxy - 5 - acetoxymercuri - 3 - methyl - 6-isopropylbenzaldehyde separate, M.pt. 120° C. These crystals contain 1 mol. of acetic acid, which is not lost on drying *in vacuo*. When treated with a solution of iodine in potassium iodide, a product is obtained which crystallises from alcohol in long, colourless needles, M.pt. 157° C. It is probably 5-iodo-4-hydroxy-3-methyl-6-isopropylbenzaldehyde.

Derivatives of Alkyl Phenols.

2-Acetoxymercuri-p-tert.-butylphenol.—Two molecules of the phenol and 1 mol. of mercuric acetate in 50 per cent. alcohol containing a little acetic acid are allowed to stand; a test portion dissolves in sodium hydroxide after about twenty hours. In three days 2·53 grams of product rich in monomercurated compound crystallises out in white needles. The filtrate on concentration gives some unchanged butylphenol, and a clear yellow oil which solidifies on standing. The latter, after steam distillation and drying, weighs 3·6 grams. It crystallises from ligroin, saturated with acetic acid, in colourless, shining plates, M.pt. 180° C.[1]

2 : 6-Diacetoxymercuri-p-tert.-butylphenol.—Six grams of the phenol in 10 c.c. of alcohol and 25·6 grams of mercuric acetate in 160 c.c. of alcohol containing 4 c.c. of acetic acid, are mixed and boiled for one hour. After standing overnight the mixture is filtered, concentrated to half-bulk, and 200 c.c. of water added. A white, sticky solid is precipitated, which becomes crystalline when warmed with alcohol. The total yield, taking into account recovery from mother-liquors, is 23·35 grams. It melts at 224° C. with decomposition, and is readily soluble in the usual organic solvents. When nitrated with concentrated acid at 0° C. it yields 2 : 6-dinitro-p-tert.-butylphenol, thus proving the positions of the mercury in the compound.

2-Acetoxymercuri-p-isoamylphenol is prepared in a similar manner to the above monomercurated product. It crystallises in white flakes, M.pt. 176° to 177° C. with decomposition.

2 : 6-Diacetoxymercuri-p-isoamylphenol crystallises from acetic acid in shining prisms, M.pt. 123° to 125° C., containing 1 mol. of

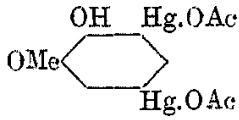
[1] Henry and Sharp, *J. Chem. Soc.*, 1926, p. 2434.

solvent. With twice its weight of ice-cold, concentrated nitric acid it yields 2 : 6-dinitro-p-isoamylphenol.

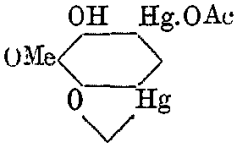
Derivatives of Guaiacol.[1]

Mercuric acetate reacts with guaiacol in methyl alcohol or ethyl alcohol—acetic acid solution to yield principally diacetoxymercuri guaiacol and possibly some monomercuri compound.

4 : 6-Diacetoxymercuri guaiacol,



forms white crystals which turn yellow, then red when heated, but do not melt. Nitric acid converts the compound to 4 : 6-dinitroguaiacol. This diacetate with 5 per cent. sodium hydroxide yields an *oxide,*



an infusible, heavy powder, turning brown at 200° to 210° C. The *chloride* is formed in the usual manner, and is a crystalline powder, decomposing at 179° to 180° C., and the *nitrate* is an infusible, white, crystalline compound.

5-Iodo-acetylguaiacol is also stated to give a *diacetate.*

Vanillin on mercuration yields a crystalline *monoacetate,* which may be converted to the *chloride,* the latter giving iodovanillin on treatment with iodine.[2]

Derivatives of Safrol.[3]

Mercuration of safrol by mercuric acetate yields a syrup containing *two isomeric acetates,* one of which eventually crystallises out, the other remaining as a sticky mass. Both isomers are reduced to safrol when treated with zinc and sodium hydroxide. The crystalline form yields a *mercurichloride,* a white crystalline powder, insoluble in water and very slightly soluble in boiling alcohol. When heated it blackens towards 170° C. The syrupy isomeric acetate yields a *chloride,* which crystallises from alcohol in rosettes of hard, glistening, prismatic needles, M.pt. 138° C. This form can be more conveniently prepared as follows : 8·1 grams of safrol in a stoppered flask are shaken with 16 grams of mercuric acetate (1 mol.) in 160 c.c. of water for about two and a half hours at 50° C. When the reaction is complete the mixture is shaken with 10 per cent. sodium chloride solution, a crystalline precipitate of the chloride being deposited. Yield about 12 grams. Recrystallisation from alcohol gives long, white, stellate, monoclinic prisms, M.pt. 136° to 137° C. The compound gives no reaction with ammonium sulphide, hydroxide, or sodium hydroxide, but if warmed with dilute hydrochloric acid the smell of safrol becomes evident. It is only slightly

[1] Mameli, *Gazzetta,* 1922, 52, ii. 23.

[2] Paolini, *Gazzetta,* 1921, 51, ii. 188.

[3] Balbiano and Paolini, *Ber.,* 1902, 35, 2998 ; *Atti. R. Accad. Lincei,* 1902, [v.], 11, ii. 65 ; *Ber.,* 1903, 36, 3579 ; Balbiano, *Ber.,* 1909, 42, 1505 ; Manchot, *Annalen,* 1920, 421, 320.

soluble in water, but easily in sodium hydroxide, from which it may be precipitated by hydrochloric acid. The compound is an *oxychloride* of the formula, $C_{10}H_{10}O_2Hg(OH)Cl$. The corresponding *bromide* is prepared in a similar way, sodium chloride being replaced by potassium bromide. It melts at 144° to 145° C., and crystallises in long, silky, shimmering, white needles from dilute alcohol. It exhibits similar properties to the chloride. The *iodide* forms small, white needles, M.pt. 152° C., which are decomposed by hydrogen sulphide, becoming first orange, then black. It does not redden when boiled with water and is unchanged by potassium iodide solution. In water it is insoluble, but readily dissolves in dilute alcohol or sodium hydroxide. The *base*, $C_{10}H_{10}O_2.Hg(OH)OH$, is easily obtained from the bromide by the action of moist silver oxide. The clear solution is faintly alkaline to litmus, but gives no colour with phenolphthalein. Treated with hydrochloric acid it becomes turbid, and on warming the mixture smells strongly of safrol. Potassium bromide solution decomposes it, with formation of the *oxybromide*.

Isosafrol reduces mercuric to mercurous acetate, and is itself oxidised to a glycol.

Derivatives of Eugenol Methyl Ether.[1]

This compound yields a syrup of mixed acetates, from which *two chlorides* may be obtained. One of these forms small, hard, white prisms, M.pt. 112° to 113° C., soluble in alcohol but insoluble in water, whilst the second isomer is resinous. The crystalline variety is best obtained as follows: Equimolecular quantities of the eugenol compound and mercuric acetate in seven times the bulk of water are heated for one hour on the water-bath, and after cooling poured into four times the volume of 3 per cent. sodium chloride solution. After standing for several days the product separates out, and on recrystallisation melts at 112·5° C. It is unchanged by ammonium sulphide or hydrate, but decomposed by warm dilute hydrochloric acid. Its constitution is given as $(OMe)_2C_6H_3-CH_2-CH=CH_2.Hg(OH)Cl$.

Apiol reacts with mercuric acetate fairly rapidly, completion of the reaction being reached in four to five hours. The *acetate* forms fine needles, M.pt. 157° to 158° C., insoluble in water but dissolving in warm alcohol. It is reduced to apiol by zinc and sodium hydroxide. Isoapiol gives an *acetate* which softens at 160° C. and melts at 174° C.

Derivatives of Resorcinol.[2]

Chloromercuri resorcinol, $C_6H_3(OH)_2.HgCl$.—To a solution of 28·3 grams of mercuric acetate (1 mol.) in 60 c.c. of water at room temperature, a solution of 29·7 grams of resorcinol (3 mols.) in 25 c.c. of water is added with frequent shaking. The reaction is completed in fifteen minutes. White flocks appear, which are filtered and quickly dissolved in concentrated sodium chloride solution, from which the chloride separates in needles. These are placed for a short time in ice, then filtered off, washed with ice-cold water, and dissolved in a large volume of ether. Removal of the solvent, and drying of the residue *in vacuo*, gives 16 grams of product. This consists of a mixture

[1] Balbiano and Paolini, *loc. cit.*; Balbiano, *loc. cit.*; Manchot, *loc. cit.*

[2] Dimroth, *Ber.*, 1902, 35, 2853; see Leys, *J. Pharm. Chim.*, 1905, [vi.], 21, 388.

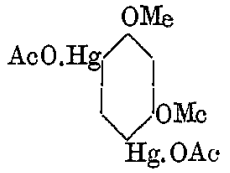
of mono and dimercurated compounds, from which the mono is removed by boiling with chloroform, in which it is soluble. From this solution prisms are deposited, M.pt. 105° C., the compound containing chloroform of crystallisation, which may be removed *in vacuo*, when the melting-point rises to 123°; at 170° the colour changes to blood red. Yield 11·7 grams. It is soluble in ether, but only with difficulty in water, the aqueous solution becoming turbid after a short time. When warmed with a little water a clear solution is obtained, but a fine yellow powder rapidly separates out and decomposes. The solution in sodium hydroxide after a short time becomes yellow, then green, then brown, and a black precipitate finally appears; these changes are accelerated by warming the solution. With ammonium sulphide the substance is immediately decomposed.

Dichloromercuri resorcinol is the insoluble residue left after the chloroform extraction, and is purified by crystallisation from ether. Yield 2·5 grams. It is a fine powder, becoming dark towards 200° C., but does not melt. In alcohol it is soluble with difficulty and is decomposed by sodium hydroxide even more rapidly than the mono compound.

4-Acetoxymercuri-2-nitroresorcinol [1] is prepared by heating together equimolecular quantities of mercuric acetate and 2-nitroresorcinol on a water-bath for thirty minutes. The orange precipitate is filtered, washed with water, alcohol, and ether, then dried over calcium chloride for forty-eight hours. Yield 75 per cent.

4-Chloromercuri-2-nitroresorcinol.—Freshly precipitated mercuric oxide and 2-nitroresorcinol suspended in water are heated on the water-bath for two hours, and the orange precipitate filtered off, washed with water, alcohol, and ether, then converted to the chloride by the addition of 10 per cent. hydrochloric acid. The product when washed and dried is a pale orange powder, soluble in dilute sodium hydroxide, methyl or ethyl alcohol, ether, benzene; only slightly in water.

4 : 6-Diacetoxymercuri-resorcinol-dimethyl ether,



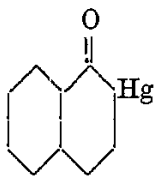
An alcoholic solution of resorcinol dimethyl ether and mercuric acetate in equimolecular proportions is boiled until the reaction is complete. On cooling, beautiful, white, feathery crystals separate. The product melts at 218° to 220° C. (corr.). It is quite stable to ammonium sulphide, the alcoholic solution giving a yellow precipitate with this reagent.[2, 3]

Derivatives of Naphthols and their Sulphonic Acids.[4]

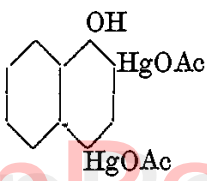
Mercuration of α-Naphthol.—When 3·6 grams of α-naphthol are dissolved in 25 c.c. of acetic acid and a solution of 8 grams of mercuric

[1] Raiziss and Proskouriakoff, *J. Amer. Chem. Soc.*, 1922, 44, 787.
[2] Kharasch and Chalkley, *J. Amer. Chem. Soc.*, 1924, 46, 1216.
[3] For mercuration of p-xylenol, monobromo-p-xylenol, 2:3-dihydroxy-1-methylbenzene and pyrogallol-1 : 3-diethyl ether, see German Patent, 250746.
[4] Brieger and Schulemann, *J. prakt. Chem.*, 1914, 89, 97.

acetate in 50 c.c. of dilute acetic acid is added, a white crystalline precipitate soon separates out, and a further quantity may be obtained from the mother-liquors. This substance does not react with ammonium sulphide, dissolves very readily in sodium hydroxide, and if more alkali is added a white crystalline precipitate appears. The body is also soluble in acetic acid, and crystals deposited from the solution when filtered off and washed with water soon become intense yellow; the addition of a drop of sodium hydroxide changes the colour from yellow to white. Its alcoholic-alkaline solutions soon decompose, but it is fairly stable towards cold sodium chloride solution, yet on heating the solution gives an alkaline reaction. Potassium bromide also gives an alkaline reaction; potassium iodide only shows a faint alkalinity at first, but suddenly mercuric iodide separates and the solution becomes strongly alkaline. The compound contains no acetoxy group, and the formula assigned to it from analysis is as follows:—



2 : 4-Diacetoxymercuri-α-naphthol,



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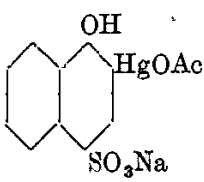
When the mercuric acetate in the preceding preparation is replaced by 16 grams of mercuric acetate in 50 c.c. of 3 per cent. acetic acid, colourless needles crystallise out in a short time, and these are filtered off and washed with water. The diacetoxy derivative is stable to ammonium sulphide, but behaves towards halogen salts in a similar way to the mono mercury compound.

2-Acetoxymercuri-1-naphthol-4-sulphonic acid (Sodium salt),

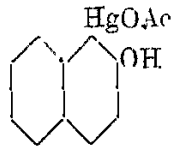


Six grams of the sodium salt of the acid in 50 c.c. of water are treated with 6·4 grams of mercuric acetate in 50 c.c. of water, and after long standing yellowish-brown bushy needles separate. These after several crystallisations from dilute acetic acid become white. The product obtained is the sodium salt of the acid, and it is very stable towards ammonium sulphide, although this stability is reduced in the presence of sodium chloride. When warmed with sodium chloride in acetic acid solution, mercury is split off. Attempts to prepare a diacetoxy compound have been unsuccessful.

1-Naphthol-5-sulphonic acid when treated with mercuric acetate gives only mercurous acetate and tarry products.

Mercuration of β-Naphthol.

1-Acetoxymercuri-β-naphthol,[1]

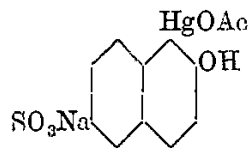


1. Twenty grams of mercuric oxide are dissolved in 520 c.c. of hot acetic acid, and on cooling, the white, glistening plates are filtered off and mixed with an acetic acid solution of 13·2 grams of β-naphthol. A heavy, crystalline precipitate separates out, and if removed, the mother-liquors give further crops on standing. Yield almost quantitative.

2. β-Naphthol (14·4 grams) is dissolved in 75 c.c. of acetic acid, and to this 32 grams of mercuric acetate in 125 c.c. of 30 per cent. acetic acid are added, when the acetoxy compound separates out.

It crystallises in white, glistening needles, which on rapid heating blacken and melt at 185° C. with violent frothing. It is only slightly soluble in the usual solvents, does not blacken with ammonium sulphide, but a yellow, voluminous precipitate separates which decomposes on heating, with deposition of mercuric sulphide. Treatment with aqueous sodium chloride yields the **1-chloromercuri** compound, which may be transformed into 1-iodo-β-naphthol.[2]

1-Acetoxymercuri-2-naphthol-6-sulphonic acid (Sodium salt),[3]



The sodium salt of Schäffer's acid (14·1 grams), containing 2 mols. of water of crystallisation, is dissolved in 100 c.c. of hot water and a solution of 16 grams of mercuric acetate in 100 c.c. of hot water added. The compound soon separates out, and is only slightly soluble in water, but readily in dilute acetic acid or sodium hydroxide. It has similar properties to the derivative from 1-naphthol-4-sulphonic acid.

1 : 8-Amidonaphthol-4 : 6-disulphonic acid (K acid) yields with mercuric chloride or acetate unstable red compounds, to which no formulæ have been assigned; the same result is obtained with its mono and dibenzoyl derivatives. 1 : 8-Amidonaphthol-3 : 6-disulphonic acid (H acid) and 1 : 8-amidonaphthol-4-sulphonic acid give colours and reactions similar to K acid, but these compounds are even more readily decomposed. Constancy of composition has not been obtained in the case of 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotrope acid), the derived compounds being orange in colour.[4]

Mercuration of Salicylyl alcohol (Saligenin).[5]—This alcohol forms a *dimercurated* compound when 1 mol. is heated with 2 mols. of mercuric acetate in alcoholic solution containing a little acetic acid. Needles separate out, from which a pure product is isolated by extract-

[1] Bamberger, *Ber.*, 1898, 31, 2624; Brieger and Schulemann, *J. prakt. Chem.*, 1914, 89, 97.

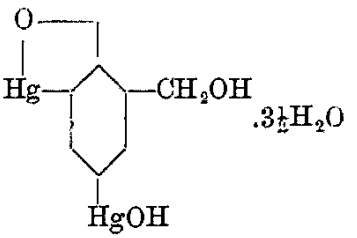
[2] Paolini, *Gazzetta*, 1921, 51, ii. 188.

[3] German Patent, 143726.

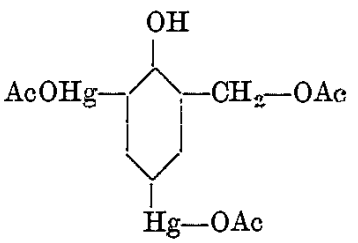
[4] For β-naphthol disulphonic acid R, see German Patent, 143448; $\beta_1\beta_3$-naphthol sulphonic acid, see German Patent, 143726.

[5] Hart and Hirschfelder, *J. Amer. Chem. Soc.*, 1920, 42, 2768.

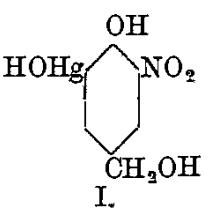
ing with water, alcohol, and ether. It is only soluble in hot glacial acetic acid or acetic anhydride and alkalies; with mineral acids it forms salts. The mercury present is non-ionic in character, and since it readily forms an anhydride is probably in the ortho position to the phenolic hydroxyl group. The following formula has been assigned to it :—



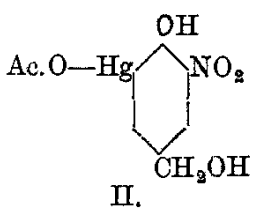
When dissolved in hot acetic anhydride it forms a *triacetate* of the composition :



Mercuration of p-Hydroxy-m-nitrophenyl carbinol.—The carbinol is prepared by the action of bromomethyl alcohol on o-nitrophenol and then treated with 2 mols. of mercuric acetate in alcohol-acetic acid solution. Fine, pale yellow needles separate, which may be recrystallised from 20 per cent. acetic acid (I.). This compound does not form an inner anhydride as in the preceding case, although the mercury is in the ortho position to the hydroxyl group. The latter fact was established by treating the compound with a solution of iodine in potassium iodide, when 3-iodo-4-hydroxy-5-nitrobenzyl alcohol is obtained.[1] Treatment with acetic anhydride yields a monoacetyl derivative (II.).



I.



II.

[1] Kharasch, *J. Amer. Chem. Soc.*, 1921, 43, 1203.

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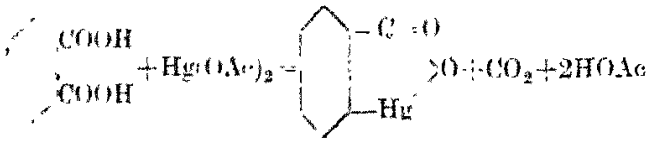
CHAPTER IX.

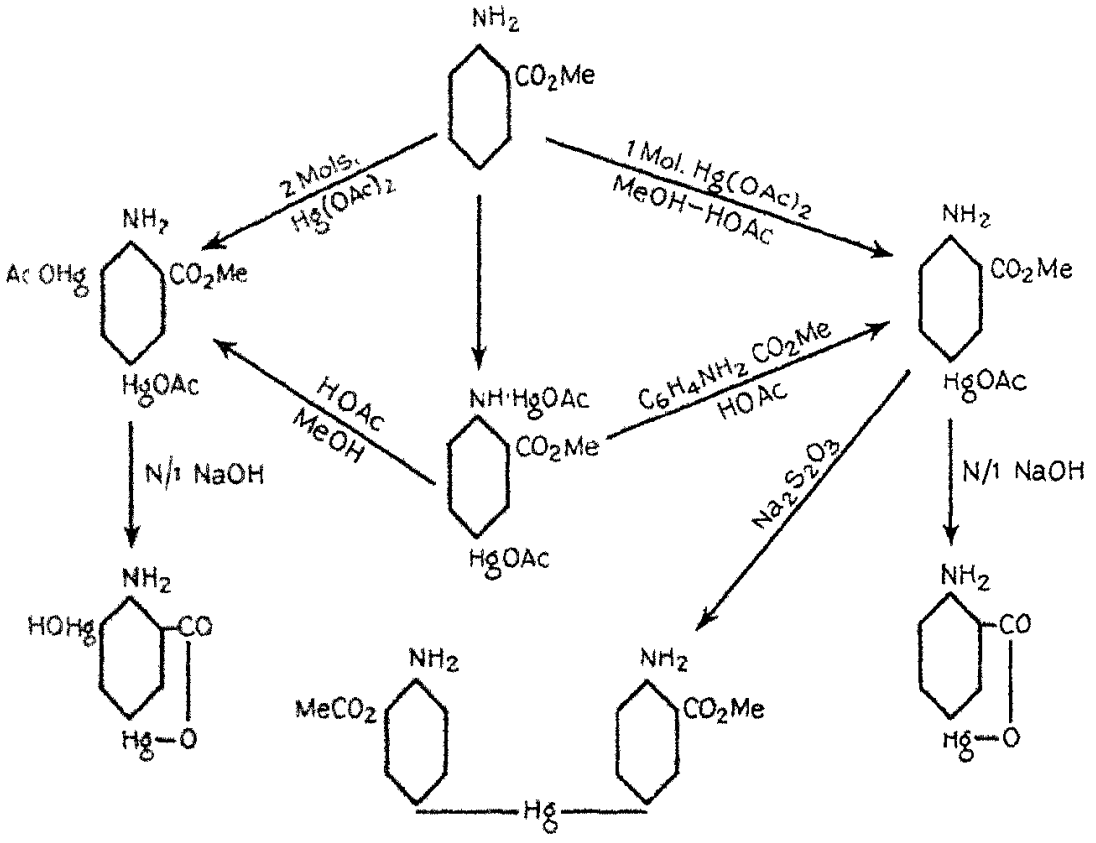
MERCURY *(continued)*.

Derivatives of Aromatic Acids.

The simplest of the aromatic acids, namely, benzoic acid, does not give an acetoxymercuri compound when heated with mercuric acetate, but only an anhydride. The position of the mercury in the ring in this case is shown to be ortho to the carboxyl group, since the same anhydride may be formed from phthalic acid, the only other products of reaction being carbon dioxide and acetic acid,



The same compound is also formed when mercuric benzoate is heated for some time at 270° C., and this method may yet become of great importance in the preparation of mercurated aromatic acids. Mercury salicylate yields an organo-mercuri anhydride, when heated for a pro-



longed period at 100° C. o-Chloromercuri-benzoic acid is obtained from the anhydride by dissolving it in concentrated sodium chloride solution, and adding acetic acid, but the p-chloromercuri compound has only been obtained by the oxidation of p-tolylmercuric chloride by alkaline permanganate. The methyl ester of benzoic acid may be mercurated in the usual way by means of mercuric acetate in the presence of a little acetic acid, and the esters of salicylic acid may be treated similarly. 5-Nitrosalicylic acid is mercurated by using an aqueous suspension of mercuric oxide at 100° C.

The interaction of mercuric acetate and anthranilic acid is more complicated than the preceding cases, and is best illustrated by the scheme on opposite page, which shows also the main reactions of the acetoxy-mercuri compounds of this acid.

A similar set of reactions has been carried out with the ethyl ester of p-aminobenzoic acid, but in addition a mercuric acetate salt of acetoxy-mercuri-p-aminobenzoic acid has been obtained, and the mono and diacetoxymercuri derivatives may be isolated from this under suitable conditions. Also in the case of this ester only the diacetoxymercuri compound has been obtained directly from the N-isodiacetoxymercuri derivative, direct mercuration being used to obtain the monoacetoxy-mercuri product.

In the mercuration of cinnamic acid and its esters, $C_6H_5.CH_2.CH_2.COOH$, the mercury residue always attaches itself to the α-carbon atom, and the solvent takes part in the reaction, attacking the β-carbon atom, alkyloxy groups becoming linked to the latter (I.). When the mercurated esters are saponified by sodium hydroxide, and the resulting product treated with sulphuric acid, water is eliminated between the hydroxy-mercuri and carboxyl groups, and an anhydride results (II.).

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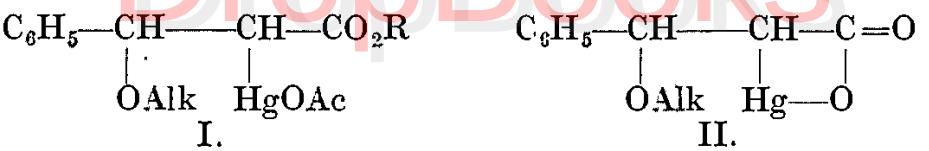


In the case of β-hydroxynaphthoic acid the mercury enters position 1, and may be removed again by the action of iodine in potassium iodide solution.

The mercuri-bis compounds of the mercurated acids have been prepared in a variety of ways. The use of sodium thiosulphate, which was given as a fairly general method in the case of mercurated amines, has only been used for acids in the preparation of the following: Mercuri-bis salicylic ethyl ester, mercuri-bis-2-aminobenzoic methyl ester, and the corresponding ethyl ester of the 4-aminobenzoic acid compound. The following sulphides yield mercuri-bis compounds by the action of heat: o-Sulphidomercuri benzoic acid, sulphidomercuri salicylic methyl ester, and the sodium salt of o-sulphidomercuri benzoic acid, the conversion in the latter case being brought about by boiling the aqueous solution. The interaction of mercuric cyanide and thiosalicylic acid in aqueous solution yields mercuri-bis-o-thiolbenzoic acid, no other organic mercury product being isolated.

o-Hydroxymercuri-p-nitrobenzoic acid has been changed to the mercuri-bis compound by treatment with alkaline stannous chloride, and in the case of the m-nitrobenzoic acid compound aluminium turnings in

alkaline solution were used. Alkaline stannous chloride has also been used for the transformation of p-chloromercuri benzoic acid.

The conversion of hydroxymercuri-salicylic acid to mercuri-bis-salicylic acid is accomplished by dissolving the compound in potassium hydroxide and treating the solution with formaldehyde sulphoxylate, and by similar means the sodium salt of mercurated hydroxybenzene sulphonic acid may be reduced.

In the case of the aminobenzoic acids, the mercuri-bis derivatives have been prepared by the reduction of the hydroxymercuri nitrobenzoic acids in neutral or alkaline solution.

An interesting formation of a mercuri-bis compound is the transformation of the anhydride of α-hydroxymercuri-β-methoxy-β-phenylpropionic acid to α-mercuri-di-β-anhydrohydroxy-β-phenylpropionic acid, by suspending the former in water and treating it with potassium iodide.

Certain mercurated acids have been tested with regard to their stability towards ammonium sulphide, with the following results: o-Chloromercuri benzoic methyl ester is only decomposed on prolonged warming, but a sulphide may be obtained by the action of methyl alcoholic hydrogen sulphide.

o-Chloromercuri benzoyl chloride in ethereal solution gives a sulphide with hydrogen sulphide only after long treatment.

The anhydride of 3-hydroxymercuri salicylic acid is decomposed when its warm solution is treated with ammonium or hydrogen sulphide.

Acetoxymercuri salicylic methyl ester yields mercuric sulphide with cold alkali sulphides.

N-Isodiacetoxymercuri-2-amino or 4-aminobenzoic acid esters when dissolved in acetic acid, and neutralised by ammonium hydroxide, are decomposed by ammonium sulphide, and a similar result is obtained when hydroxymercuri-2- or 4-aminobenzoic anhydrides are dissolved in ammonium hydroxide and treated with ammonium sulphide. The sodium salt of 2 : 2′-mercuri-bis-4-aminobenzoic acid is stable to hydrogen sulphide, and acetoxymercuri-4-aminobenzoic ethyl ester only yields mercuric sulphide when boiled for a long time with ammonium sulphide.

The anhydride of α-hydroxymercuri-β-hydroxy-β-phenylpropionic acid in alkaline solutions only yields mercuric sulphide on long standing with ammonium sulphide; but if the β-hydroxy group be replaced by β-methoxy, the decomposition takes place immediately.

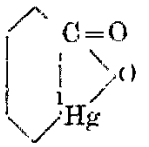
α-Mercuri-di-β-anhydrohydroxy-β-phenylpropionic acid is not decomposed by ammonium sulphide.

The following compounds when heated with hydrochloric acid yield mercuric chloride and an organic acid: The anhydride of o-hydroxymercuri benzoic acid and the anhydride of α-hydroxymercuri-β-hydroxy-β-phenylpropionic acid, whilst o-chloromercuri benzoic methyl ester is decomposed by halogen acids, and cold dilute hydrochloric acid eliminates the acetoxymercuri group attached to the nitrogen in N-isodiacetoxymercuri anthranilic methyl ester.

Derivatives of Benzoic Acid and its Esters.[1]

Anhydride of o-hydroxymercuri benzoic acid may be prepared as follows :—

[1] Dimroth, *Ber.*, 1902, 35, 2853; Pesci, *Atti. R. Accad. Lincei*, 1900, [v.], 9, i. 255; 1901, [v.], 10, i. 362, 413; Whitmore and Woodward, *J. Amer. Chem. Soc.*, 1926, 48, 533; Sachs, *Ber.*, 1920, 53, [B], 1737.



1. Mercuric benzoate is heated in an oil-bath to 270° C. until a test portion gives no precipitate of mercuric oxide when treated with sodium hydroxide. The melt is cooled, powdered, and washed with alcohol and ether to free it from benzoic acid. It is then dissolved in a small amount of dilute sodium carbonate and carbon dioxide passed through the solution, the anhydride being precipitated as a white powder.

2. Mercuric acetate is heated with benzoic acid until no mercuric oxide is obtained by adding sodium hydroxide to a test portion. The melt is then treated with ammonium hydroxide to form the ammonium salt, from which the anhydride is isolated by adding acetic acid.

3. Sodium phthalate solution, mercuric acetate, and a little acetic acid are boiled for some time, when the anhydride is precipitated. The acid is only slightly soluble in all organic solvents, but readily soluble in dilute alkali or sodium carbonate. The latter solution gives a white precipitate with lead acetate, and blue-green with copper acetate. Treatment with sodium chloride yields the sodium salt of o-chloromercuri benzoic acid, but boiling with hydrochloric acid gives benzoic acid and mercuric chloride. Bromine reacts with the anhydride, forming o-bromobenzoic acid, and this, together with the fact that the anhydride can be prepared from sodium phthalate, prove that the mercury is in the ortho position. Pesci states that he also prepared the following salts : *Ammonium, isoamyl* and *benzylammonium, barium, calcium*, and *magnesium*. Also bromo- and iodo-mercuri benzoic acids are stated to have been prepared.[1] The sodium salt at 150° C. reacts with ethyl mercaptan according to the equation :

$$ClHg.C_6H_4.CO_2H + HSEt = C_6H_5.CO_2H + ClHg.SEt^2.$$

o-Chloromercuri benzoic acid.—The crude anhydride obtained by Pesci [3] is dissolved in concentrated sodium chloride and acetic acid added. The precipitate is recrystallised from much hot water. It melts with decomposition between 222° and 238° C. With ethyl mercaptan it yields ethylthiomercuric chloride, EtS.HgCl. The *sodium* salt of the acid in acetone solution gives, with ethyl mercaptan, *o-mercaptomercuribenzoic acid*, according to the equation :

$$C_6H_4\begin{cases}CO_2Na\\HgCl\end{cases} + HSEt = C_6H_4\begin{cases}CO_2H\\Hg.SEt\end{cases} + NaCl$$

The compound may be recrystallised from acetone, and partly melts at 138·5° to 140° C. with decomposition.

p-Chloromercuric benzoic acid is obtained from p-tolylmercuric chloride by oxidation with alkaline permanganate. It is a white amorphous powder which it is impossible to purify. Treatment with alcoholic iodine yields p-iodobenzoic acid. Boiling with dilute alcoholic sodium hydroxide gives *sodium p-hydroxymercuribenzoate*. The latter salt with aqueous sodium bromide or iodide yields *sodium p-bromo*

[1] See German Patent, 229575. [2] Sachs, *Ber.*, 1920, 53, [B], 1737.
[3] Pesci, *loc. cit.*

and *p-iodomercuribenzoate* respectively. The chloro compound reacts with phosphorous pentachloride in chloroform, giving the *acid chloride*, the latter on boiling with n-butyl alcohol yielding *p-chloromercuribenzoic acid n-butyl ester.*

o-Mercuri-bis-benzoic acid[1] may be obtained either by boiling an aqueous solution of the sodium salt of o-sulphidomercuri benzoic acid, $S(Hg.C_6H_4.CO_2Na)_2$, or by saponification of o-mercuri-bis-benzoic methyl ester. It crystallises from alcohol in shining needles, insoluble in water, decomposing when heated, without melting.

p-Mercuri-bis-benzoic acid.[2]—p-Chloromercuribenzoic acid is dissolved in sodium hydroxide and treated with stannous chloride. The *sodium* salt is very soluble in water.

o-Chloromercuribenzoic methyl ester.[3]—Twenty grams of finely powdered mercuric acetate, 20 grams of benzoic methyl ester, and 3 grams of acetic acid are gently boiled, the reaction taking three to four hours for completion. The mixture is filtered and evaporated *in vacuo*. 19 grams of a yellowish oil being obtained. Acetone is added until no further precipitate is formed, the latter consisting of 5·6 grams of diacetoxymercuri compound. The acetone filtrate on evaporation yields 13·3 grams of yellow resin, which is mainly a mono substitution product. It is dissolved in dilute alcohol and treated with sodium chloride, when 9·1 grams of the o-chloromercuri compound are deposited. It is fairly soluble in the usual organic solvents, insoluble in water or petroleum ether. From dilute alcohol or ethyl acetate it crystallises in needles, sintering at 142° C. and melting at 162° C. Ammonium sulphide only splits off the mercury on prolonged warming, but halogen acids, especially hydriodic acid, readily decompose it. Stannous chloride in alkaline solution immediately reacts, metallic mercury separating.

When the chloride is dissolved in warm methyl alcohol, and treated with a methyl alcoholic solution of hydrogen sulphide ($\frac{1}{2}$ mol.), which has been saturated at about 2° C., a white amorphous precipitate of *sulphidomercuribenzoic methyl ester* is obtained. The quantity of hydrogen sulphide present is controlled by titration, as excess dissolves the sulphide. It is easily soluble in chloroform, benzene, or aniline, but only slightly in other organic solvents.

o-Mercuri-bis-benzoic methyl ester, $Hg(C_6H_4.COOMe)_2$.—Seven grams of the above sulphide are heated for three hours at 120° C., then cooled, powdered, and extracted with ethyl acetate. Spontaneous evaporation of the solution gives 4·1 grams of white crystals. Yield 90 per cent. When saponified it gives o-mercuri-bis-benzoic acid.

o-Chloromercuribenzoyl chloride.[4]—Five grams of the anhydride of o-hydroxymercuribenzoic acid is treated with 15 grams of thionyl chloride, when a vigorous reaction takes place accompanied by frothing. The solid after filtration consists of microscopic needles and an amorphous product, extraction with benzene leaving the bulk of the latter behind. From the benzene solution 3·5 grams of substance are obtained, which does not completely melt at 173·5° C. Prolonged treatment with hydrogen sulphide in ethereal solution gives *o-sulphidomercuribenzoyl*

[1] Schoeller, Schrauth, and Heuter, *Ber.*, 1920, 53, [B], 638; Pesci, *Atti. R. Accad. Lincei*, 1900, [v.], 9, i. 255; 1901, [v.], 10, i. 362 413.
[2] Whitmore and Woodward, *J. Amer. Chem. Soc.*, 1926, 48, 533.
[3] Schoeller, Scrauth, and Heuter, *loc. cit.* [4] Sachs, *Ber.*, 1920, 53, [B], 1737.

chloride, $S(HgC_6H_4.COCl)_2$, which remains unmelted at 230° C. When boiled with methyl alcohol, the sulphide produces o-chloromercuri benzoic methyl ester.

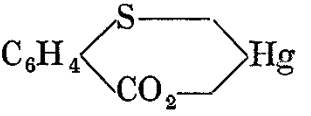
o-Chloromercuri thiobenzoic ethyl ester is obtained from chloromercuribenzoyl chloride by dissolving it in hot benzene, and adding ethyl mercaptan in benzene solution through a dropping funnel. It crystallises from alcohol in pale yellow, microscopic, rhomboidal plates, M.pt. 142·5° to 144·5° C., soluble in ether, benzene, chloroform, or acetone. Its constitution is probably represented by

$$ClHg.C_6H_4.CO.SEt.$$

Derivatives of Thiolbenzoic Acid.

Mercuri-bis-o-thiolbenzoic acid, $Hg(S.C_6H_4.CO_2H)_2$,[1] is prepared by the interaction of mercuric cyanide and thiosalicylic acid in aqueous solution. It crystallises in needles, M.pt. 256° C., and is practically insoluble in water and the usual organic solvents.

Anhydride of hydroxymercuri thiolbenzoic acid,



A solution of thiosalicylic acid in alcohol is treated with water until faint turbidity is produced, then an aqueous solution of mercuric acetate (1·5 mols.) slowly added. The precipitate is boiled with alcohol to remove impurities, then treated with a mixture of ammonium hydroxide and carbonate until complete solution is obtained. The latter is filtered hot, and treated with acetic acid until faintly opalescent. On cooling, the anhydride crystallises in pale yellow, microscopic rods. Yield 50 per cent. When boiled with a concentrated solution of sodium chloride, and the solution filtered and treated with acetic acid, impure *o-chloromercuri thiolbenzoic acid* is precipitated. When the latter compound or the anhydride are dissolved in concentrated ammonium hydroxide, a substance crystallising in plates, M.pt. 206° C. with decomposition, is produced. Its formula corresponds to $C_{14}H_{16}O_6N_2S_2Hg_3$. Some mercuri-bis thiolbenzoic acid is also formed.

Derivatives of Nitrobenzoic Acids.

o-Mercuri-bis-p-nitrobenzoic acid.[2]—o-Hydroxymercuri-p-nitrobenzoic acid (115 grams) is dissolved in about 1500 c.c. of water with the aid of sodium hydroxide, and treated with an alkaline solution of 100 to 150 grams of stannous chloride, until a filtered test on the addition of stannous chloride gives no mercury. The mixture is then warmed for a time to complete the reaction and filtered. The filtrate is acidified with hydrochloric acid, the compound coming down as a yellow powder. It is soluble in water or alcohol, but not in benzene, toluene, ethyl acetate, or mineral acids. The *sodium* salt is a yellow powder, soluble in water, the solution giving precipitates with practically all metallic salts.

A similar type of compound has been obtained from *m-nitrobenzoic*

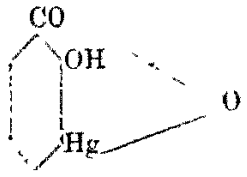
[1] Sachs and Blessl, *Ber.*, 1925, 58, [B], 1497.
[2] German Patent, 251332.

acid. The reduction in this case is carried out with aluminium turnings in alkaline solution. The compound has similar properties to the above.

Phenol disulphonic acid and mercuric acetate in equimolecular proportions react to give a compound containing about 40 per cent. of mercury. It is soluble in water and does not precipitate albumen in the cold.[1]

Derivatives of Salicylic Acid and its Esters.

Anhydride of 3-Hydroxymercuri-salicylic acid,



When dry mercury salicylate is heated for a long time at 100° C. it is found that a test portion no longer gives a precipitate with sodium hydroxide. If the reaction be carried out at 120° C. the change takes place more rapidly, and the same product is obtained when equimolecular proportions of freshly precipitated mercuric oxide and salicylic acid are heated for a long time on the water-bath in aqueous solution.[2] It forms a white mass, soluble in alkali, but cannot be crystallised from solvents, and is decomposed on heating, without melting. When warmed with hydrogen sulphide or alkali sulphides it undergoes decomposition. The hydroxymercuri group is replaced by the action of iodine, o-iodo-salicylic acid being formed, this proving that the mercury occupies the ortho position to the hydroxyl group. The compound has been purified by treating it with ammonium carbonate solution, when the *ammonium* salt is formed, $HO.Hg.C_6H_3.OH.CO_2NH_4$, and decomposing this by dilute acetic acid.[3]

3-Chloromercuri-salicylic acid, $ClHg.C_6H_3.OH.COOH$.—This acid is obtained from the corresponding sodium or calcium salts by the addition of dilute acetic acid. It crystallises in needles from boiling water or methyl alcohol. The *sodium* and *potassium* salts are known, and the *lithium* salt is prepared from the anhydride and lithium chloride solution. Both this and the *calcium* salt form thin needles, which are more soluble in cold than hot water. *Bromomercuri-salicylic acid*, obtained by the interaction of the acid and potassium bromide, is precipitated by acetic acid, and forms colourless crystals, insoluble in water, but slightly soluble in boiling alcohol. The corresponding *iodomercuri acid* has also been described.

Mercuri-bis-salicylic acid.[4]—The anhydride of hydroxy mercuri salicylic acid (33·6 parts) is dissolved in 5·6 parts of potassium hydroxide in 300 parts of water, and a solution of 7·7 parts of sodium

[1] The following patents also deal with benzoic acids: German Patent, 23914, o-chlorobenzoic acid, o-iodobenzoic acid, o-toluic acid. *Ibid.*, 249332, addition to above; 1:4-dimethyl-2-benzoic acid, trimethylbenzoic acid, 3:4-dimethoxybenzoic acid, 3:5-dibromobenzoic acid. *Ibid.*, 234054, 261875, o-chlorobenzoic acid. *Ibid.*, 290210, sodium m-sulphobenzoate. *Ibid.*, 407669, 413835, p-benzyloxybenzoic anhydride and similar compounds.

[2] Dimroth, *Ber.*, 1902, 35, 2873.

[3] Buroni, *Gazzetta*, 1902, 32, ii. 305, 311; *Chem. Zentr.*, 1903, i. 578; Brieger, *Arch. Pharm.*, 1912, 250, 62; *Chem. Zentr.*, 1912, i. 753.

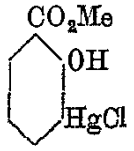
[4] German Patent, 255030.

formaldehyde sulphoxylate in about 100 parts of water added with stirring. The mixture is left until clear, filtered, and treated with dilute acid. The white precipitate is dissolved in sodium hydroxide and changed to the *sodium* salt, which may be obtained in the solid form by evaporation *in vacuo*. The free acid is a white, heavy, water-insoluble powder. It has no melting-point, but decomposes at high temperatures. It yields salts with alkalies or alkali carbonates.

By a similar method of reduction a mercuri-bis compound may be obtained from mercurated 2-hydroxybenzene sulphonic acid (sodium salt).

More recent investigators [1] contend that salicylic acid can only be mercurated to give pure products when mercuric sulphate is used. A mixture of the *anhydrides* of *o-* and *p-hydroxymercuri-salicylic acids* is formed, the latter yielding *p-thiocyanomercuri-salicylic acid* with potassium or ammonium thiocyanates, and *sodium p-sodium sulphitomercuri-salicylate* with sodium sulphite.

3-Chloromercuri-salicylic methyl ester,



The ester is obtained by adding sodium chloride to the mother-liquors obtained in the preparation of the acetoxy compound described below, from which 6 grams of substance are obtainable. It is soluble in alcohol, but in other organic solvents less soluble than the acetate.

Acetoxymercuri-salicylic methyl ester.—Fifteen grams of mercuric acetate, an equal weight of the ester, and 2·5 grams of acetic acid are boiled under reflux for about forty minutes, until the reaction is complete. On cooling, needles separate, and after standing overnight these are filtered off. Yield 9 grams, 52 per cent. It melts at 202° C. (corr.) and is readily soluble in warm alcohols, ethyl acetate, acetone, or chloroform, but with difficulty in water or petroleum ether. In alkali it is soluble, but the ester is saponified.

Sulphidomercuri-salicylic methyl ester, $S(Hg.C_6H_3.OH.COOMe)_2$.—To a cold, saturated, alcoholic solution containing 10 grams of the acetoxy ester, 35 c.c. of an alkali hydrogen sulphide solution saturated at 20° C. are added dropwise. This is the requisite quantity required to form the neutral sulphide, and excess should be avoided or an acid sulphide is formed, which is markedly soluble. The precipitate is filtered off, pressed on a tile and dried *in vacuo*, 7·5 grams (85 per cent.) of a white powder being obtained. It is soluble in chloroform, benzene, aniline, dilute aqueous alkali or alkali sulphides.

Mercuri-bis-salicylic methyl ester, $Hg(C_6H_3.OH.CO_2Me)_2$.—Ten grams of the above sulphide are heated for six hours at 110° C., and the mass powdered and extracted with 120 c.c. of ethyl acetate, 0·8 gram, 12 per cent., of the ester being isolated. It is soluble in the usual solvents and melts at 170° to 180° C. (corr.).

Acetoxymercuri-salicylic ethyl ester.—This product is not so readily formed as the methyl ester, but if the reaction is carried out at 180° C. the yield is almost quantitative. It crystallises from ethyl

[1] Rupp and Gersch, *Arch. Pharm.*, 1927, 265, 323.

acetate-ligroin mixture in needles, sintering at 200° C. and melting at 206° C. (corr.).

When 12 grams of the acetate are powdered and dissolved in 120 c.c. of cold, saturated sodium thiosulphate solution, a precipitate is immediately thrown down. This is filtered after six hours and dried. It consists of *mercuri-bis-salicylic ethyl ester*. 6·2 grams, 82 per cent., yield. It melts at 193° C. (corr.) and has similar properties and solubilities to the methyl compound.

3-Chloromercuri-5-nitrosalicylic acid.[1]—5-Nitrosalicylic acid is heated with 2 mols. of freshly precipitated mercuric oxide in aqueous suspension for twelve hours at 100° C. The resulting orange product is filtered, washed, and dried. When warmed with alkali, part of the mercury is split off as mercuric oxide and is filtered off. The solution is cooled, filtered, and acidified with hydrochloric acid, when a precipitate consisting of mono and dimercurated derivatives is thrown down. This is treated with boiling 50 per cent. methyl alcohol, when the mono compound goes into solution, and the mixture is filtered through a hot-water funnel. Both compounds are thus isolated, the mono-chloro compound melting at 235° C. and the dichloro at 238° C.

Diacetoxymercuri-5-nitrosalicylic acid is obtained by heating 5-nitrosalicylic acid with 2 mols. of mercuric oxide in hot glacial acetic acid, filtering whilst hot and cooling, when white crystals are deposited. These are recrystallised from acetic acid and become pale yellow when dry.

Several *cyanomercuri-salicylic acids* have recently been described, but difference of opinion seems to obtain regarding their mode of formation.[2, 3]

Derivatives of Anthranilic Acid.[4]

N-Isodiacetoxymercuri-anthranilic methyl ester.—One gram of anthranilic methyl ester is added to a solution of 2·4 grams of mercuric acetate dissolved in 25 c.c. of 80 per cent. methyl alcohol. Flocks separate in a few minutes, and after about 1·5 hours no mercury ions can be detected when tested for by sodium hydroxide. If allowed to stand for a long time the crystals become yellow and change to acetoxymercuri-anthranilic ester, according to the scheme shown below in (I.). To remove any by-products from the iso compound it is thoroughly washed with methyl alcohol and dried with ether. When its acetic acid solution is neutralised by ammonium hydroxide, then treated with ammonium sulphide, a precipitate of mercuric sulphide is deposited, showing that the mercury residue is substituted in the amino group. When digested with cold dilute hydrochloric acid, an acetoxymercuri group is split off, and chloromercuri anthranilic acid

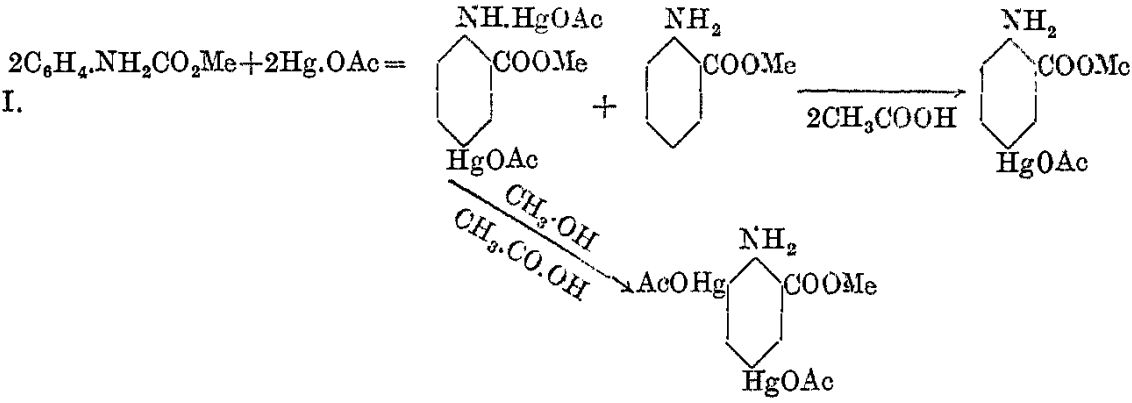
[1] Raiziss and Proskouriakoff, *J. Amer. Chem. Soc.*, 1922, 44, 787.

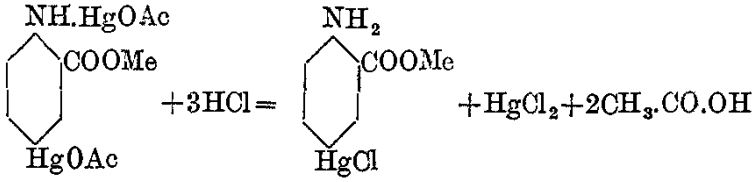
[2] Boedecker and Wunstorf, *Arch. Pharm.*, 1925, 263, 430; Gersch, *ibid.*, 1926, 264, 88.

[3] The following German patents taken out in 1909 deal with the mercuration of salicylic acid derivatives: 224435, 224864, 227391, 229574, 229575, 229781. *Ibid.*, 261875, o-chlorobenzoic acid, salicylic acid. German Patent, 30511, British Patent, 161922 (1909), hydroxymercuri salicylic anhydrides. German Patent, 216267, salicylsulphonic acid (COOH : OH : SO_2H = 1 : 2 : 5). *Ibid.*, 248291, glycol ester of salicyllo acid.

[4] Schoeller and Hueter, *Ber.*, 1914, 47, 1930.

methyl ester is formed (II.). The iso compound is soluble in ammonium hydroxide, acetic acid, hot water, and hot alcohols, but insoluble in acetone, chloroform, benzene, or petroleum ether. The hot aqueous or alcoholic solutions set to a jelly on cooling.

I. 

II. 

Acetoxymercuri-anthranilic methyl ester may be obtained:

1. From the preceding N-iso-diacetoxy compound. 2·5 grams of the latter are suspended in 15 c.c. of methyl alcohol and 0·6 gram (1 mol.) of methyl anthranilate in 2 c.c. of acetic acid added, the whole being heated for thirty minutes on the water-bath. The mass is then allowed to stand for twenty-four hours in the ice-chest, filtered, and dried *in vacuo* over sulphuric acid. Yield 2·6 grams.

2. Nine grams of methyl anthranilate is added to a warm solution of 22·5 grams of mercuric acetate (1 mol.) in 100 c.c. of methyl alcohol containing 10 c.c. of acetic acid. After fifteen minutes' heating at 50° C. the reaction is complete, and the product is cooled overnight in ice, when the ester crystallises out in pale yellow needles. These are filtered and washed with methyl alcohol and dry ether. Yield 22 grams, 90 per cent. The crystals melt to a yellow liquid at 178° to 180° C., which decomposes at 180° to 182° C. The compound is readily soluble in boiling water, hot alcohols, or acetic acid, sparingly soluble in benzene, ethyl acetate or acetone, very slightly soluble in chloroform or petroleum ether.

Diacetoxymercuri-anthranilic methyl ester results as follows :—

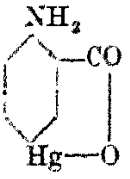
1. Three grams of the N-iso compound are heated with 2·5 grams of acetic acid in 20 c.c. of methyl alcohol for about an hour at 50° C. The mixture is cooled to 0° C., filtered, washed with methyl alcohol, and dried. Yield 2·6 grams, M.pt. 218° to 220° C.

2. Methyl anthranilate (1 mol.) is heated with 2 mols. of mercuric acetate in methyl alcohol-acetic acid mixture at 50° C. until a test gives no reaction with ammonium sulphide. The product thus obtained melts at 221° to 222° C., is soluble in the usual organic solvents, but less readily than the mono-substitution products. The structural formula is shown above.

Chloromercuri-anthranilic methyl ester is obtained, as previously stated, by treating the N-iso compound with cold dilute

hydrochloric acid. It also results by the addition of aqueous sodium chloride to an alcoholic solution of the acetoxymercuri compound. It forms small needles or rods, M.pt. 184° C., soluble in the usual organic solvents. The corresponding *bromide* crystallises in fine needles, M.pt. 178° (darkening); the *iodide* sinters at 172° C., melting at 173° to 174° C. to a brown liquid.

Hydroxymercuri anthranilic anhydride,



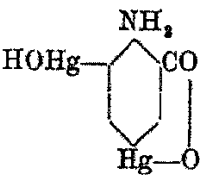
This compound is obtained as follows :—

1. The monoacetoxy compound in aqueous suspension and 2·25 mols. of Normal sodium hydroxide are boiled for a short time, when the acetate group is split off, the sodium salt of hydroxymercuri anthranilic acid being formed. The cooled solution is treated with cold Normal sulphuric acid, the anhydride being precipitated, filtered, washed with water, and dried.

2. Steam is blown through an equimolecular mixture of pure anthranilic acid and yellow mercuric oxide for two to three hours, until a test portion gives a clear solution in alkali. The product is purified by solution in sodium hydroxide and precipitation by sulphuric acid. Yield 96 per cent.

The compound is a faint yellow, amorphous powder. Prep. 1 has M.pt. 212° to 214° C. (darkening). Prep. 2 has M.pt. 210° C. It is readily soluble in aqueous potassium iodide, cyanide, or sodium thiosulphate, not so easily in potassium bromide, and still less in potassium chloride; rather insoluble in the usual organic solvents. When dissolved in caustic alkali or carbonates it may be precipitated unchanged by acids. Aqueous alkaline solution gives, with aqueous solutions of heavy metal salts, a corresponding salt in the form of an amorphous precipitate. The *copper* salt is a bright green substance. The ammoniacal solution when treated with ammonium sulphide and warmed gives a deposit of mercuric sulphide. If the hydroxy compound be treated with potassium iodide in aqueous solution, *iodomercuri-anthranilic acid* is deposited as a white powder on the addition of the calculated amount of sulphuric acid; but if iodine in potassium iodide be used, iodoanthranilic acid is produced.

Dihydroxymercuri-anthranilic anhydride,

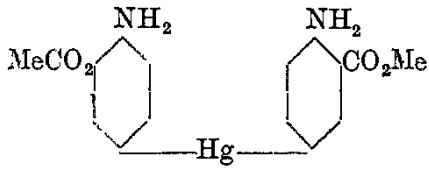


This substance is prepared in the same way as the preceding anhydride, using the diacetoxymercuri compound as the starting material. It is a pale yellowish-green, amorphous powder.

Acetoxymercuri-acetylanthranilic methyl ester, $AcOHg.C_6H_3(NHAc).CO_2Me$.—The acetylated ester is heated with mercuric acetate

in an oil-bath for thirty minutes at 120° to 130° C. The excess of ester is then extracted with ether and the mercury compound recrystallised from very dilute alcohol. It crystallises in glistening plates, M.pt. 212° C., extremely soluble in all organic solvents except ether or petroleum. If the above reaction be carried out in cold methyl alcohol solution, only a 10 per cent. yield is obtained in 1·5 days, but two hours' boiling in aqueous solution or seven hours in methyl alcohol completes the reaction. The alcoholic mother-liquors from the crystallisation, when treated with sodium chloride, give the corresponding *chloride*, fine needles from boiling ethyl acetate, M.pt. 245° to 246° C.

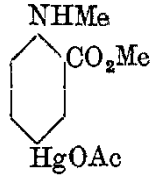
Mercuri-bis-anthranilic methyl ester,



Ten grams of the acetate in a 75 per cent. alcohol solution are treated with a very concentrated aqueous solution containing about 20 grams of sodium thiosulphate. A white, amorphous precipitate at once appears, and the mixture is raised to 45° C. and maintained at that temperature for about 1·5 hours. The product is then evaporated *in vacuo*, when 7·5 grams of dry substance are obtained. It is purified by dissolving in ethyl acetate, filtering, concentrating the solution, then adding petroleum ether dropwise until the mixture becomes opalescent. On intense cooling, light yellow needles are deposited (4·5 grams, 65 per cent.). The ester melts at 196° to 197° C. (corr.) with darkening. It is soluble in the usual solvents, with the exception of water and petroleum ether.[1]

DropBooks

Acetoxymercuri-methylanthranilic methyl ester,



The ester is obtained in 97 per cent. yield by adding the methyl ester of methyl anthranilic acid to mercuric acetate solution in methyl alcohol, the reaction being complete in about thirty minutes. It forms fine needles, M.pt. 200° C., easily soluble in chloroform, hot acetic acid, boiling alcohols, ethyl acetate, acetone, or benzol, slightly soluble in cold water.

The corresponding *chloromercuri* compound crystallises in white needles, M.pt. 210° to 212° C., becoming violet; the *bromide* has M.pt. 215° C., turning violet; *iodide*, needles, M.pt. 190° to 191° C., darkening at 185° C.

Hydroxymercuri-methylanthranilic anhydride.—Prepared in the usual manner from the acetoxymercuri compound it is obtained in 99·2 per cent. yield. It is a greenish-yellow, amorphous precipitate, decomposing at 203° C. When prepared from methylanthranilic acid and yellow mercuric oxide the reaction is complete in fifteen minutes.

[1] Schoeller, Schrauth, and Hueter, *Ber.*, 1920, 53, [B], 642.

The *iodomercuri-methylanthranilic acid* may be prepared from it. It is more stable towards acids than the unmethylated compound, and is insoluble in the usual organic solvents.

Acetoxymercuri-ethylanthranilic ethyl ester, M.pt. 178° C. (decomp.), is soluble in the usual solvents on warming, and crystallises from alcohol in needles, the corresponding *methyl ester* forming needles, M.pt. 189° C.

Acetoxymercuri-dimethylanthranilic methyl ester forms thick, prismatic crystals from methyl alcohol. M.pt. 134° C., and is easily soluble in the common solvents. Prepared in the usual way the reaction is complete in about three hours. The *chloride* forms strongly refracting prisms, M.pt. 162° to 163° C.; the *bromide*, white needles, M.pt. 164° C.; *iodide*, thick prisms, M.pt. 159° C.; the chloride and bromide contain 1 mol. of water of crystallisation.

Sulphatomercuri-dimethylanthranilic acid, $SO_4(HgC_6H_3.NMe_2.CO_2H)_2.3H_2O$.—The acetoxy compound is boiled for fifteen minutes with Normal sodium hydroxide, and the solution treated with Normal sulphuric acid. After cooling for twenty-four hours in ice, thick prisms are obtained, which on crystallisation from alcohol form small, white needles. These contain 3 mols. of water, and when heated slowly decompose towards 180° C. It is easily soluble in hot water, but insoluble in the usual organic solvents. It should be noted that when other acetoxymercuri compounds are treated in the above manner the anhydrides are isolated.

The *chloromercuri* derivative is prepared by saponifying the acetoxy compound and adding Normal hydrochloric acid. It crystallises from boiling water in prisms, M.pt. 175° C. with decomposition, and is sparingly soluble in organic solvents.

6 : 6'-Mercuri-bis-2-aminobenzoic acid.—From 30 grams of mercury o-nitrobenzoate treated in the same way as the para compound, 27·5 grams of the anhydride of hydroxymercuri-o-nitrobenzoic acid are isolated. This is then reduced with ferrous carbonate as before. The product is pale yellow, easily soluble in acids or alkalies, and has no definite melting-point.[1]

Derivatives of Meta-aminobenzoic Acid.

From **m-Acetaminobenzoic acid.**[2]—m-Acetaminobenzoic acid (53 grams) in sodium hydroxide is treated with a solution of 48 grams of mercuric acetate. The precipitate is the mercury salt of m-acetaminobenzoic acid, which is dried and heated at 150° to 175° C. until a test gives a clear solution in sodium hydroxide. The melt is extracted with boiling alcohol, the residue dissolved in sodium hydroxide, and the compound precipitated by hydrochloric acid. It is filtered, dried, and recrystallised from methyl alcohol. It forms white needles, melting about 200° C., very easily soluble in alkalies. From the aqueous solution of the sodium salt other salts may be obtained in the usual way. The constitution is as follows :—

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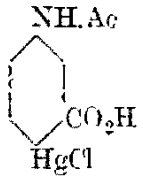
[1] The following deal with mercurated anthranilic acids: German Patent, 234054, anthranilic acid. *Ibid.*, 248291, methyl ester of methylanthranilic acid.

[2] German Patent, 264338.

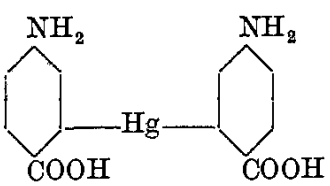


The method may be varied by heating m-acetaminobenzoic acid with mercuric oxide in an oil-bath, first at 210° C. until the product becomes grey, then for a further two hours at 220° C. If the mercuric oxide be replaced by the acetate, heating at 180° C. for three to four hours will complete the reaction.

In a similar way the corresponding *m-benzoylaminobenzoic acid* derivative is prepared. It melts at about 220° C. with decomposition, and has properties similar to the acetyl compound.

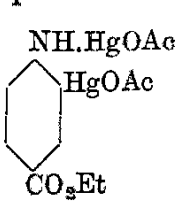
Mercuri-bis-3-aminobenzoic acid.—m-Nitrobenzoic acid and mercuric oxide are heated at 200° C. until the reaction is complete. The result is the mercurated nitro compound, and this is reduced in neutral solution with aluminium-mercury couple at 40° to 50° C. to the amine. It has similar properties to the para compound.

From **p-Aminobenzoic acid: 2:2′-Mercuri-bis-4-aminobenzoic acid.**[1]—Seventy-five grams of the mercury salt of p-nitrobenzoic acid is heated at about 225° C. until a test of the reaction product gives a clear solution in sodium hydroxide. This usually takes about three hours. The mass is then cooled, extracted with alcohol, and dried. The dry product (38 grams) is dissolved in about 600 grams of 15 per cent. sodium hydroxide and boiled. The boiling solution is treated with a solution of ferrous sulphate to bring about the reduction, approximately 225 grams of the iron salt being required. The mixture is filtered and the filtrate strongly acidified with hydrochloric acid, the compound separating as a voluminous precipitate. It is insoluble in the usual solvents, but dissolves in alkalies or hot hydrochloric acid, a crystalline *hydrochloride* separating from the latter in fine, microscopic needles. The *sodium* salt of the acid is a pale yellow, crystalline powder, easily soluble in water, the solution becoming brown on standing for a long time. When hydrogen sulphide is passed through the solution no mercuric sulphide is precipitated. The constitution is as follows :—



It may also be obtained by alkaline or neutral reduction of the derivatives of hydroxymercuri-p-nitrobenzoic acid.[2]

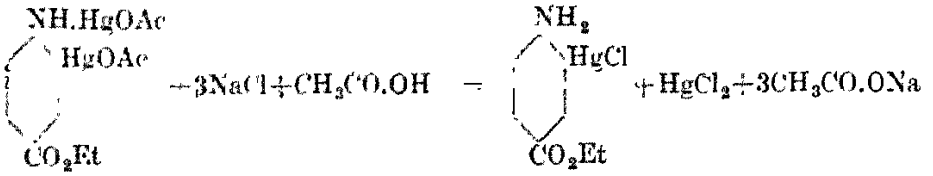
N-Isodiacetoxymercuri-p-aminobenzoic ethyl ester.[3]—



[1] German Patent, 249725.
[2] See Blumenthal and Oppenheim, *Biochem. Zeit.*, 1913, 57, 261.
[3] Schoeller, Schrauth, and Liese, *Ber.*, 1919, 52, [B], 1777.

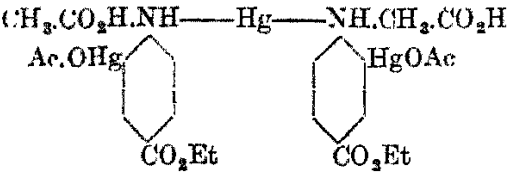
Two grams of the ethyl ester (1 mol.) in 10 c.c. of methyl alcohol are added to 8 grams of mercuric acetate (2 mols.) in 50 c.c. of the same solvent, and the mixture allowed to stand for a day. A pale yellow, non-crystalline product separates out, and this is filtered and washed with methyl alcohol and ether. Yield 7·7 grams, 93 per cent. It cannot be recrystallised, melts about 245° C., and is soluble in ammonium hydroxide, acetic acid or mineral acids, but with decomposition in the latter; in the usual organic solvents it is practically insoluble. Its acetic acid solution after neutralisation with ammonium hydroxide splits off mercuric sulphide when treated with cold ammonium sulphide.

When dissolved in acetic acid-methyl alcohol mixture and warmed, then treated with aqueous sodium chloride, *chloromercuri-p-aminobenzoic ethyl ester* is precipitated.



The same product may be obtained by treating the acetate with sodium chloride. The yield by the first method is 94 per cent., and when recrystallised from ethyl acetate the M.pt. is 223° C.

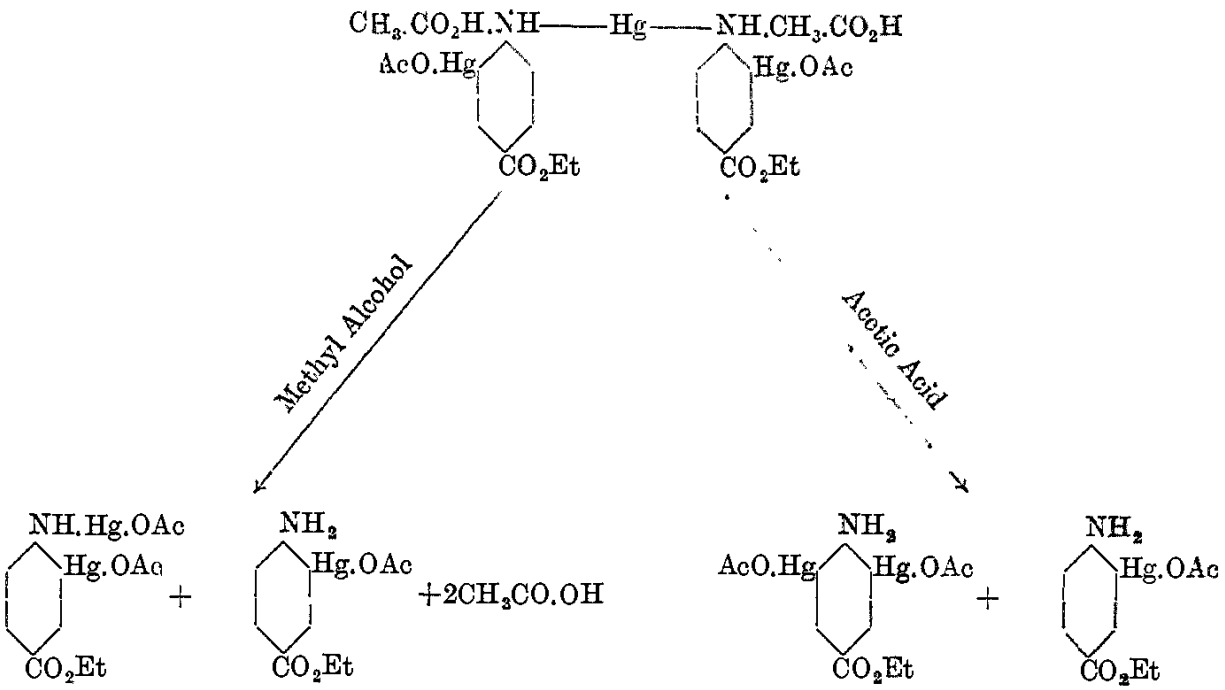
Mercuric acetate salt of acetoxymercuri-p-aminobenzoic acid ethyl ester,



Four grams of the ethyl ester of p-aminobenzoic acid in 8 c.c. of methyl alcohol are mixed with 8·4 c.c. of mercuric acetate in 16 c.c. of methyl alcohol and 8 c.c. of acetic acid. The salt soon separates, and is filtered and washed with alcohol and ether. Yield 8 grams. It forms microscopic, rhombic crystals, M.pt. 230° to 240° C., is soluble in ammonium hydroxide or acids with decomposition, and to a slight extent in cold methyl alcohol, ethyl acetate, or acetone. Ammonium sulphide decomposes it in the cold. When the substance is dissolved in methyl alcohol containing a small quantity of acetic acid, treated with dilute acetic acid, then with Normal sodium chloride solution, *chloromercuri-p-aminobenzoic ethyl ester* is precipitated. The filtrate is made alkaline with ammonium hydroxide, and the solution saturated with hydrogen sulphide, mercuric sulphide being obtained in a quantity corresponding to one-third of the mercury originally present in the mercuric acetate salt.

When the substance is boiled with methyl alcohol for about two hours, N-isodiacetoxymercuri-p-aminobenzoic ethyl ester separates out, and if the mother-liquors are diluted with water, acetoxymercuri-p-aminobenzoic acid ethyl ester, M.pt. 228° C., is obtained.

If the methyl alcohol in the above operation be replaced by acetic acid, the resulting products are the mono- and diacetoxymercuri compounds. These changes are shown below :

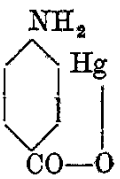


Acetoxymercuri-p-aminobenzoic ethyl ester.—A mixture of 3 grams of the ethyl ester and 6·3 grams of mercuric acetate is heated in a glycerine bath. At 130° C. the mass becomes liquid and acetic acid is evolved, and as the temperature rises to 160° C. the melt solidifies. The product is cooled, pulverised, and extracted with methyl alcohol, the solution partly evaporated and diluted with hot water. The acetate crystallises in shining, bushy needles as the solution cools. Yield 2·3 grams.

Using the same quantity of starting material and carrying out the mercuration in acetic acid solution, the reaction takes twenty-four hours, and 3·3 grams of product are isolated. Both methods give a certain amount of diacetoxymercuri derivative, which remains behind during the methyl alcohol extraction.

The compound melts at 182° C., then solidifies, and melts again at 228° C. It is only slightly soluble in ether or petroleum ether, but soluble in other organic solvents. With ammonium sulphide it gives a yellow *sulphide*, but prolonged boiling with this reagent precipitates black mercuric sulphide. It is converted to the *chloromercuri* compound when treated with sodium chloride.

Hydroxymercuri-p-aminobenzoic anhydride,



The preceding acetoxymercuri compound (3·1 grams) is powdered, suspended in 40 c.c. of water and boiled for a short time with 16·5 c.c. of Normal sodium hydroxide (2·25 mols.). The addition of 9·2 c.c. (1·25 mols.) of Normal sulphuric acid precipitates the anhydride in white flocks, excess of acid being avoided or the anhydride will dissolve, forming salts. Yield 2·4 grams. It is only slightly soluble in the usual solvents. The ammoniacal solution gives mercuric sulphide, if warmed with ammonium sulphide. It dissolves in water, and aqueous solutions

of potassium chloride, iodide, or sodium thiosulphate; whilst in bases it is soluble, forming salts.

Diacetoxymercuri-p-aminobenzoic ethyl ester.—One method of preparation has already been mentioned and two others are available. (*a*) By heating the N-iso compound with acetic acid; (*b*) 1 gram of the ethyl ester in 3 c.c. of acetic acid is treated with 4·2 grams (2 mols.) of mercuric acetate in 10 c.c. of the same solvent. After several days the crystals are filtered off and washed with methyl alcohol and ether. Yield 1·4 grams. It melts at 255° to 257° C., and is rather insoluble, except in acetic acid or ethyl acetate. Heating with acetic anhydride in acetic acid solution produces an *acetyl* derivative, fine needles from dilute alcohol. M.pt. 247° C. The addition of hot Normal sodium chloride solution to the compound in methyl alcohol-acetic acid mixture gives a theoretical yield of the *dichloromercuri* compound. It crystallises in small needles, which melt at about 270° C.[1]

Mercuri-bis-p-aminobenzoic ethyl ester, $Hg(C_6H_3.NH_2.CO.OEt)_2$.- The corresponding chloromercuri body is heated with aqueous sodium thiosulphate, a flocculent precipitate soon forming. This crystallises from ethyl acetate in shining needles, M.pt. 176° C.[2]

Derivatives of Cinnamic Acid and its Esters.

Bülmann [3] has shown that when the malenoid forms of compounds containing olefine linkages contain two negative groups, they react with mercuric salts to form complex mercury compounds. Since allocinnamic acid reacts with mercuric chloride in this manner, whilst ordinary cinnamic acid does not, the conclusion has been drawn that the allocinnamic acid has the *cis* configuration.

Anhydride of α-hydroxymercuri-β-hydroxy-β-phenylpropionic acid,[4]

$$C_6H_5-\underset{OH}{CH}-\underset{Hg}{CH}-\underset{\overset{1}{O}}{C=O}$$

This substance is prepared by adding a hot solution of mercuric acetate to a boiling aqueous solution of allocinnamic acid. It crystallises in colourless microscopic crystals, which have neutral properties. Its alkaline solutions are not affected by ammonium sulphide, unless allowed to stand for a considerable time, when mercuric sulphide separates out. When heated with hydrochloric acid, mercuric chloride and ordinary cinnamic acid are produced. The anhydride reacts with potassium iodide according to the equation :

$$HO.CHC_6H_5.CH\begin{cases}CO_2\\|\\Hg\end{cases}+2KI+H_2O=HO.CHC_6H_5.CH_2.COOK+HgI_2+KOH$$

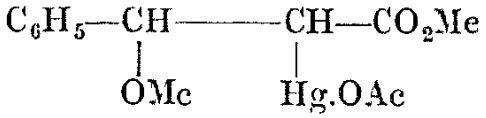
[1] p-Aminobenzoic acid isobutyl ester is dealt with in German Patent, 248291.

[2] For mechanism of mercuration of 3-acetamino-4-hydroxybenzoate and sodium aminobenzoates, see Maschuraun, *Annalen*, 1926, 450, 85, 98. For diaminodiphenyldicarboxylic acids, see Blumenthal, *Biochem. Zeit.*, 1911, 32, 59; 1912, 39, 50; 1914, 65, 460; *Chem. Zentr.*, 1911, i. 1523; 1912, i. 1631; 1914, i. 1245. Arylaminosulphonic acids are dealt with in German Patent, 281009. Sulphophenol carboxylic acids, German Patent, 410969.

[3] Bülmann, *Ber.*, 1902, 35, 2756.

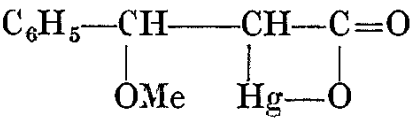
[4] Bülmann and Bjerrum, *Ber.*, 1910, 43, 568.

α-Acetoxymercuri-β-methoxy-β-phenylpropionic methyl ester,[1]



Mercuric acetate (19·6 grams) is dissolved in 100 to 120 c.c. of warm methyl alcohol and 10 grams of methyl cinnamate stirred in. After six hours the reaction is complete, and in two days 18 grams of product are obtained. Yield 65 per cent. It is easily soluble in the usual organic solvents, and crystallises from ethyl acetate in warty needles, M.pt. 140·5° C. (corr.); from methyl alcohol spear-shaped crystals are deposited which change in four to six days to prisms. The acetoxymercuri group reacts in the usual way with alkali halides, forming a *chloride*, short needles, M.pt. 133·5° C. (corr.); *bromide*, needles, M.pt. 110·5° C.; *iodide*, needles, M.pt. 100° C. The acetoxymercuri group may also be replaced by sodium diethylbarbiturate when the corresponding veronal compound is formed.

Anhydride of α-hydroxymercuri-β-methoxy-β-phenylpropionic acid,



This derivative is obtained in a pure state when the preceding compound is saponified by heating with Normal sodium hydroxide and then Normal sulphuric acid added. It decomposes at about 187° C., and its solution in ammonium hydroxide yields mercuric sulphide immediately when treated with ammonium sulphide, whilst its alkali solutions give precipitates with aqueous solutions of the salts of heavy metals.

α-Acetoxymercuri-β-ethoxy-β-phenylpropionic methyl ester.—The preparation is carried out as for the methoxy compound, but the methyl alcohol is in this case replaced by ethyl alcohol. It crystallises from ethyl acetate in long needles, M.pt. 123° C., easily soluble in most organic solvents. When treated with alcoholic ammonium sulphide, β-ethoxy-β-phenylpropionic methyl ester is formed, as a colourless oil, B.pt. 256° C. (corr.).[2] The *chloride* crystallises in needles, M.pt. 114° C.; the *bromide* in small needles, M.pt. 85° C.; the *iodide* in small prisms, M.pt. 71° C. The *internal anhydride* may be prepared by warming 3 grams of ester with 15 c.c. of Normal sodium hydroxide until a clear solution is obtained, and then adding 10 c.c. of Normal sulphuric acid. It decomposes at 191° C. (corr.).

The following derivatives are prepared in a similar manner to the methoxy compound and the change of alkyloxy group is brought about by carrying out the mercuration in the corresponding alcohol.

α-Acetoxymercuri-β-propoxy-β-phenylpropionic methyl ester yields white, matted needles, M.pt. 135·5° C. (corr.), very soluble in the usual solvents. The yield is about 71 per cent. after two weeks' standing. The *chloride*, *bromide*, and *iodide* crystallise in needles, melting at 109°, 84°, and 84° C. respectively. The *internal anhydride* decomposes at 188° C. (corr.).

α-Acetoxymercuri-β-isopropoxy-β-phenylpropionic methyl

[1] Schrauth, Schoeller, and Struensee, *Ber.*, 1910, 43, 695.
[2] Schrauth, Schoeller, and Struensee, *Ber.*, 1911, 44, 1048, 1432.

ester occurs as white, felted needles, M.pt. 150° C. (corr.); the *anhydride* decomposes at 191° C.

α-Acetoxymercuri-β-isobutoxy-β-phenylpropionic methyl ester yields white needles, M.pt. 154° C. (corr.), the reaction taking eight days for completion. The *anhydride* decomposes at 193° C. (corr.).

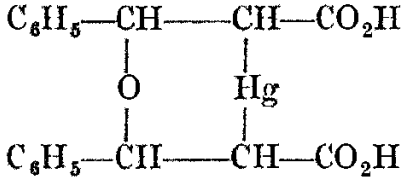
α-Acetoxymercuri-β-methoxy-β-phenylpropionic ethyl ester is much more difficult to obtain than the methyl ester, the reacting substances being allowed to stand for twelve days before being removed. The compound crystallises in prisms, M.pt. 107° C.; yield 45 per cent. A similar yield of the corresponding *benzyl ester* may be obtained in a few days. This substance crystallises in long, silky needles, M.pt. 127° C.[1]

A compound has also been obtained from allyl cinnamate by treating it with 2 mols. of mercuric acetate in methyl alcohol solution. Sodium chloride solution is added, and the oil which first separates solidifies on standing. The formula assigned to the substance is

$$C_6H_5.OMeCH.CH(HgCl).CO_2CH_2.CHOMe.CH_2HgCl$$

It is readily soluble in alcohol, chloroform, benzene, or ethyl acetate, and is precipitated from its sodium hydroxide solution by sulphuric acid.

α-Mercuri-di-β-anhydrohydroxy-β-phenylpropionic acid.—When the anhydride of α-hydroxymercuri-β-methoxy-β-phenylpropionic acid is moistened with alcohol, then suspended in water, and potassium iodide added until a solution is obtained, the addition of Normal sulphuric acid gives a white, flocculent precipitate. It crystallises from alcohol in shining rhombic leaflets, M.pt. 200° C. with decomposition. It acts as a dibasic acid, and does not yield mercuric sulphide when treated with ammonium sulphide. Probable constitution:



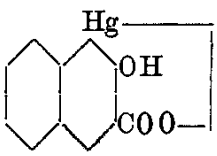
α-Acetoxymercuri-β-methoxy-β-phenylpropionic l-menthyl ester.[2]—l-Menthyl cinnamate in methyl alcohol is treated with mercuric acetate in the usual way. It melts at 95° to 105° C. and gives the value, $[\alpha]_D^{21}$ −23·1° in chloroform solution.

When the compound is treated with sodium bromide in methyl alcohol solution, the *α-bromomercuri derivative* is formed. This has been isolated as two optical isomerides: the first has M.pt. 145° to 146° C., $[\alpha]_D^{25}$ −48·6°; the second has M.pt. 134° to 135° C., $[\alpha]_D^{25}$ +61·9°. Similarly the *iodide* is obtained as a mixture of the two isomerides, M.pt. 126° to 128° C., $[\alpha]_D^{25}$ +65·89°, and M.pt. 102° to 103° C., $[\alpha]_D^{25}$ −24·27° respectively. Only one *chloride*, however, has been obtained, M.pt. 150° to 152° C., $[\alpha]_D^{25}$ −45·08°.[3]

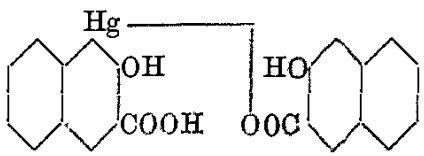
From β-Hydroxynaphthoic acid.[4]—To a boiling solution of 1·88 grams of β-hydroxynaphthoic acid in 25 c.c. of 96 per cent. alcohol, a solution of 3·2 grams of mercuric acetate in 25 c.c. of boiling water is

[1] See German Patent, 228877.
[2] Sandborn and Marvel, *J. Amer. Chem. Soc.*, 1926, 48, 1409.
[3] The following deal with *tyrosine*: German Patents, 267411, 267412, 279957.
[4] Brieger and Schulemann, *J. prakt. Chem.*, 1914, 89, 97.

added with shaking. A yellowish-white precipitate is obtained which is readily soluble in sodium hydroxide, but not acted upon by cold ammonium sulphide. This is filtered and washed first with 96 per cent. alcohol, then with much water and dried over calcium chloride *in vacuo*. The preparation is a pale yellow, fine powder, insoluble in all organic solvents. It is soluble in alkali, imparting a pale yellow colour to the solution. This solution when treated with stannous chloride gives metallic mercury. It therefore contains no preparation of the type R—Hg—R. With iodine in potassium iodide the mercury is removed, and a compound of β-hydroxynaphthoic acid formed. Since the analysis for mercury is somewhat low in compound I., it has been suggested that salt formation takes place between the mercurated product and the excess of acid present, giving compound II., as excess of naphthoic acid cannot be removed by careful washing with alcohol. The same compound is also obtained when the acid is mercurated by means of mercuric oxide. The above facts are represented by the following formulæ :—



I.



II.

A dimercurihydroxy naphthoic acid cannot be obtained, and mercuration of β-hydroxynaphthoic-4 : 7-disulphonic acid has not been very successful.

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CHAPTER X.

MERCURY (*continued*).

Miscellaneous Mercury Derivatives of Organic Compounds.

MERCURY COMPOUNDS DERIVED FROM OLEFINES.

The compounds formed from the ethylenes have given rise to considerable discussion. The formulæ assigned to them are very complex, and no two investigators seem in agreement as to their constitution. This is probably due to experiments not being carried out under standard conditions. Hofmann and Sand [1] divide the compounds obtained by the action of ethylene on mercuric salts into the following types :—

1. Ethene mercury salts, $CH_2{=}CH.HgX$
2. Polymerised ethene mercury salts, $(C_2H_3HgX)_n$
3. Ethanol mercury salts, $OH.CH_2.CH_2.HgX$
4. Ethyl ether mercury salts, $O(CH_2.CH_2.HgX)_2$

The formation of these types is explained on the assumption that the mercuric salt, HgX_2, ionises into HgX and X ions, which combine with the ethylene to form $CH_2X.CH_2.HgX$. If such a compound loses its hydrogen halide it forms an ethene compound. Hydrolysis of the compound would form an ethanol salt, whilst partial hydrolysis and coupling with the original compound would give the ether type, if hydrogen halide were lost.

They draw the following distinction between ethanol salts (I) and ether salts (II) :—

1. An alkaline solution of (I) in potassium iodide remains clear, but (II) gives a white precipitate.

2. An alkaline solution of (I) gives a white precipitate with potassium sulphide, soluble in hot potassium hydroxide: (II) gives a white precipitate, insoluble in boiling potassium hydroxide.

3. The halogen-free alkaline solutions of ether salts yield insoluble carbonates, whilst the ethanol salts do not.

Manchot and his co-workers have criticised the above types and consider them to be molecular addition compounds. Their arguments will be found when discussing the respective compounds.

In the case of the acetylene compounds very little satisfactory work has been accomplished, and with both ethylenes and acetylenes only such work as has given more or less definite results has been included in the following pages.

The references given on the next page should be taken along with those given in the text by anyone desiring a more complete knowledge of the work done on these compounds.

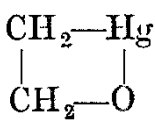
[1] Hofmann and Sand, *Ber.*, 1900, 33, 1340, 2692.

Ethylene,[1] *butylene and amylene,*[2] *acetylene,*[3] *isopropyl acetylene.*[4]

Ethanol mercuric chloride, $CH_2OH.CH_2.HgCl$.[5] –Ethylene is passed into a nearly saturated solution of mercuric chloride, and a double salt of the ethanol compound with mercuric chloride is obtained. This is washed free from other compounds and recrystallised from spirit. It forms plates, soluble in potassium hydroxide, from which solution carbon dioxide precipitates ethanol mercuric chloride. The chloride is also formed by the action of ethylene on saturated mercuric acetate, treating the solution, with potassium chloride, then precipitating the compound by carbon dioxide. It melts at 155° C.

This compound with potassium cyanide or concentrated acids (not acetic acid) yields ethylene. From an aqueous solution of the chloride, hydrogen sulphide precipitates all the mercury as sulphide, but from an alkaline solution potassium hydrosulphide precipitates *ethanol mercuric sulphide* $(CH_2OHCH_2Hg)_2S$.

Ethanol mercuric bromide is prepared in a similar manner to the chloride. It has also been formed from the mother-liquor obtained in the production of ethanol mercuric sulphate by the action of ethylene on mercuric sulphate. The liquor is saturated with ammonia, then treated with acetic acid, the grey-black residue filtered off and potassium bromide added to the filtrate, the bromide separating out.[6] It crystallises from alcohol in thin, glistening plates, M.pt. 158° C., which yield ethylene when treated with 20 per cent. hydrochloric acid at 15° C. A similar result takes place with 30 per cent. acetic acid, the reaction becoming more rapid on heating. Cold sodium and ammonium hydroxides give clear solutions from which ammonium sulphide throws down a white precipitate. By bromine in alcohol, the bromide is oxidised to bromomercuri acetic acid, $HgBr.CH_2.COOH$. Sodium ethylate with an alcoholic solution of the bromide precipitates a white powder,



which melts indefinitely at 146° C., is soluble in water and alkali, from which solution dilute acids give a white precipitate.

Evaporation of the bromide with acetic anhydride gives an acetyl derivative, $HgBr.CH_2.CH_2.OAc$, lustrous leaflets, M.pt. 75° C., which with hydrochloric acid yield ethylene.

When oxidised by permanganate the bromide is converted mainly into oxalic acid, bromomercuri acetic acid being formed at the same time.[7]

[1] Sand and Breest, *Zeitsch. anorg. Chem.*, 1907, 59, 424; Sand, *Ber.*, 1901, 34, 1385; *Annalen*, 1903, 329, 138.

[2] Denigès, *Bull. Soc. chim.*, 1898, [3], 19, 494.

[3] Plimpton, *Proc. Chem. Soc.*, 1892, 8, 110; Keiser, *Amer. Chem. J.*, 1893, 15, 537; Plimpton and Travers, *Trans. Chem. Soc.*, 1894, 65, 266; Biginelli, *Chem. Zentr.*, 1898, i. 925; Le Comte, *J. Pharm. Chim.*, 1902, [6], 16, 297; *Chem. Zentr.*, 1902, ii. 1499; Burkard and Travers, *Trans. Chem. Soc.*, 1902, 81, 1270; Biltz, *Ber.*, 1905, 38, 133; Brame, *Trans. Chem. Soc.*, 1905, 87, 427; Nieuwland and Maguire, *J. Amer. Chem. Soc.*, 1906, 28, 1025; French Patent, 479656, *Chem. Abs.*, 1914, 11, 870; Swiss Patent, 74446, *Chem. Abs.*, 2027; Patents *Chem. Abs.*, 1918, 12, 42, 280, 484, 566, 588.

[4] Perkin, *Chem. Abs.*, 1913, 7, 2095; British Patent, 277 (1913).

[5] Hofmann and Sand, *Ber.*, 1900, 33, 1340, 2692.

[6] Blilmann, *Ber.*, 1900, 33, 1641.

[7] Sand and Singer, *Annalen*, 1903, 329, 166.

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Ethanol mercuric sulphate, $(CH_2OH.CH_2.Hg)_2SO_4$.—Ethylene is passed into a solution of mercuric sulphate, and the sulphate is precipitated as a white crystalline body. It is easily soluble in warm water, not decomposed on boiling with ammonium hydroxide, and gives a white precipitate with ammonium sulphide. Although stable to boiling alkali, it is decomposed by boiling acid, mercuric sulphate being formed. Concentrated hydrochloric acid decomposes it with the evolution of ethylene.

Ethene mercuric iodide, $CH_2=CH-Hg-I$.—A solution of mercuric nitrate is treated with potassium hydroxide until a slight precipitate is formed. The latter is then dissolved by passing in ethylene, more potassium hydroxide is added to give a precipitate and more ethylene passed in. This process is repeated until no more ethylene is absorbed. Potassium iodide solution is added and carbon dioxide passed in, glistening silver plates of the iodide being precipitated. It melts at 147° C., is easily soluble in hot alcohol and fairly soluble in hot water. It is decomposed by hydrochloric acid or potassium cyanide with evolution of ethylene. Boiling with mercuric oxide and potassium hydroxide yields the insoluble form of dimercuri acetic acid, (HOHg)(Hg)C.COOH.[1] The iodide is easily soluble in alcoholic potash, either the *hydroxide*, $CH_2=CH.HgOH$, or the *anhydride*, $\begin{array}{|l}CH_2.CH_2.Hg.O,\\ \hline\end{array}$ being formed, and the alkaline solution of this compound when boiled with methyl iodide regenerates the iodide. At 150° C. methyl iodide decomposes the iodide, forming mercuric iodide and hydrocarbon. Reduction in alkaline solution by sodium amalgam or electrolysis gives ethyl alcohol.[2] When ethanol mercuric chloride in methyl alcohol solution is treated with silver nitrate, *ethene mercury nitrate* is formed, $CH_2=CH.HgNO_3$. It crystallises in strongly refracting plates, easily soluble in water and exploding when heated. The addition of a little dilute hydrochloric acid to the aqueous solution precipitates ethanol mercuric chloride.

Ethyl ether mercuric chloride, $(HgCl.CH_2.CH_2)_2O$.—Ethylene is passed into a nearly neutral solution of mercuric sulphate, a sulphate of composition $C_6Hg_4(SO_4)_2O_1H_{10}$ being precipitated. This is dissolved in 10 per cent. potassium hydroxide, potassium chloride added, and carbon dioxide passed in. The precipitated chloride melts at about 190° C., is slightly soluble in water, alcohol, or ether. The corresponding *bromide* is obtained by substituting potassium bromide for the chloride. It is a fine, white powder, has a similar solubility to the chloride, and sinters above 200° C. It only reacts very slowly with dilute hydrochloric or acetic acid, whereas the ethanol salt is readily attacked. It dissolves in sodium hydroxide, forming a clear solution.

An alkaline solution of the sulphate when treated with carbon dioxide yields the *carbonate*, $[(Hg.CH_2.CH_2)_2O]CO_2$.

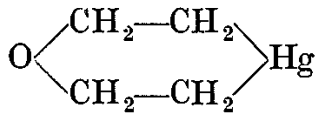
An *ethene mercuric iodide* of the polymerised type $(C_2H_3HgI)_x$ is formed by the action of potassium iodide on the sulphate. It crystallises from alkali in platelets, M.pt. 161° C.

An analogous *sulphide* is obtained from an alkaline solution of the sulphate by the action of potassium hydrosulphide. It is a white precipitate, unchanged by boiling with water, and is insoluble in hot potassium hydroxide.

[1] Hofmann and Sand, *Ber.*, 1901, 34, 1385, 2906.
[2] Sand and Singer, *Ber.*, 1902, 35, 3180

Mercurodiethylene oxide, $O:(C_2H_4)_2:Hg_2$.[1]—Ethyl ether mercuric bromide dissolved in 10 per cent. potassium hydroxide is treated with an alkaline stannite solution until no further precipitate is obtained. The grey-violet product is decanted, washed, and dried over sulphuric acid. Yield nearly quantitative. It is a bluish-black precipitate, sintering at 80° C. and melting at 140° to 150° C., insoluble in water, alkalies, and the usual organic solvents. It is completely decomposed by hot hydrochloric acid, and when heated with benzene in a sealed tube at 140° C. is converted into mercury and the mercuric compound.

Mercuridiethylene oxide,



Prepared as just described, it crystallises from benzene in glistening, colourless needles, M.pt. 145° C., insoluble in water, alkali, or dilute mineral acids, but readily soluble in most organic solvents, except ether and acetone. It is not decomposed when heated with potassium hydroxide, iodide, or cyanide, but with fuming hydrochloric acid it gives a theoretical yield of ethylene.[2]

Manchot and Klüg [3] criticise the above work of Hofmann and Sand, and advance arguments against the structures given above, in favour of additive formulæ. Their points are :

1. Hofmann and Sand's formula does not explain why the compound of the type $CH_2OH.CH_2.HgX$ is immediately decomposed by halogen acids with the evolution of ethylene, whereas it is stable towards other acids. According to Manchot, a similar result is obtained by potassium cyanide or thiocyanate in the presence of acids.

2. The reaction is caused by all those substances which combine with mercuric halides to yield additive compounds of the type $HgCl_2.2HCl$, and may be expressed by the equations :

$$C_2H_4.OH.HgCl+HCl.\rightleftharpoons C_2H_4.HgCl_2+H_2O$$

and

$$C_2H_4.HgCl_2+2HCl\rightleftharpoons HgCl_2.2HCl+C_2H_4$$

3. It was shown by Sand that the complex $C_2H_4.Hg(OH)$ is univalent and that the dichromate was prepared by Manchot and expressed as

$$[C_2H_4.Hg(OH)]_2Cr_2O_7$$

4. The decomposition by iodine of the ethylenic compounds containing mercury is more readily explained by the additive formula. It is assumed that the iodine displaces the oxygen, followed by the addition of oxygen at the double bond, thus yielding $CH_2I.CH_2.OH$ and $O(CH_2.CH_2I)_2$ respectively.

5. According to Sand's formula, the ethanol mercuric iodide should yield propyl alcohol when treated with methyl iodide, whereas methyl alcohol, ethylene, and mercuric iodide are obtained.

[1] Sand, *Ber.*, 1901, 34, 2910.
[2] Stoehr, *J. prakt. Chem.*, 1897, [2], 55, 80.
[3] Manchot and Klüg, *Annalen*, 1920, 420, 170.

6. Ethyl ether mercuric salts yield ethylene when heated with methyl iodide at 110° C.,

$$2C_2H_4.HgI.O.HgI + 2CH_3I = 2C_2H_4 + 2HgI_2 + (CH_3)_2O$$

and this is also advanced to support the additive structure.

Acetoxymercuri-ethyl methyl ether, $AcOHg.CH_2.CH_2.OMe$.[1]—Mercuric acetate (20 grams, 85 per cent.) is shaken with 100 c.c. of methyl alcohol, and air-free ethylene passed in. The absorption is measured, and in one hour at 22° C. and 760 mm., 1460 c.c. of ethylene are absorbed. When the reaction is complete the mixture is distilled under reduced pressure to remove the alcohol and acetic acid, and a yellow, oily liquid remains. This after standing for twenty-four hours *in vacuo* over sulphuric acid and caustic alkali solidifies (17 grams). Yield 82 per cent. It crystallises from petroleum ether in fine needles, M.pt. 42° C., easily soluble in water and the usual solvents. Treated with a little hydrochloric acid in aqueous solution it yields the *chloride*, but with excess of hydrochloric acid ethylene is evolved on gentle warming. With ammonium sulphide a white amorphous *sulphide* is precipitated which splits off mercuric sulphide on warming. Sodium stannite solution gives metallic mercury in the cold. The acetate decolorises permanganate and ethereal iodine solutions.

The *bromide* is obtained by treating the alcoholic acetate with aqueous potassium bromide. It crystallises in small bushes of white needles, M.pt. 58° C., which are readily soluble in all the usual solvents, except light petroleum. The corresponding *iodide* crystallises in white needles or plates, not particularly stable.

Acetoxymercuri-dimethyl ether is prepared in the same way as the preceding compound, but the reaction takes longer to complete. Yield 95 per cent. It forms fine white needles, sintering at 33° C. and melting at 36° C. The *chloride* yields white needles, M.pt. 92° C., and when heated with methyl iodide at 100° C. practically 1 mol. of ethylene is produced and mercuric iodide formed.

Since these compounds are readily decomposed by halogen acids yielding ethylene, and the latter is evolved when they are treated with alkyl iodides, the following constitution has been proposed [2]:

$$C_2H_4.Hg(OEt)X$$

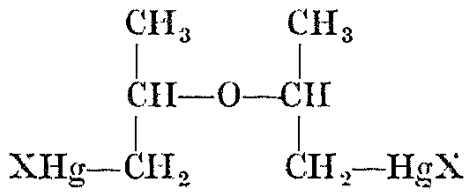
Propanol mercuric chloride,[3] $CH_3.CHOH.CH_2.HgCl$.—Propylene is passed into an alkaline solution of mercuric nitrate, and the required amount of potassium chloride added. After twelve hours, carbon dioxide is passed in and the solution extracted with ether. It crystallises from this solvent in prisms, melting at about 53° C. Instead of using mercuric nitrate, the acetate may be used, but not the sulphate, as a yellow precipitate is then obtained which contains much basic sulphate.

The corresponding *bromide* is prepared similarly to the chloride, but in this case the salt is precipitated by the carbon dioxide. It is recrystallised from absolute alcohol-ether mixture and melts at 76° C. The *iodide* crystallises in needles, M.pt. 68° C., from benzene or ether. It is easily soluble in absolute alcohol, sparingly in carbon disulphide,

[1] Schoeller, Schrauth, and Essers, *Ber.*, 1913, 46, 2864.
[2] Manchot, *Ber.*, 1920. 53, [B], 984.
[3] Sand and Hofmann, *Ber.*, 1900, 33, 1353; Sand and Genssler, *ibid.*, 1903, 36, 3699.

benzene, or water. When an alkaline solution of the chloride or bromide is treated with hydrogen sulphide, a white *sulphide* is precipitated, this in time dissolving with the formation of a *hydrosulphide*.

Dibromomercuri-di-isopropyl ether is obtained by dissolving the bromide in alcohol and passing carbon dioxide into the solution. It may be purified by solution in pure potassium hydroxide and precipitation by carbon dioxide. It is a heavy, crystalline powder, insoluble in organic solvents, and has no melting-point. When dissolved in alkali and treated with potassium iodide solution, the *iodide* is obtained. This may be recrystallised from boiling potassium hydroxide. It has similar properties to the bromide. The structure of these compounds is as follows :—



Butanol mercuric chloride.[1]—Isobutylene, $(CH_3)_2C{=}CH_2$, containing a little pseudobutylene, $CH_3.CH{=}CH.CH_3$, when passed into an aqueous solution of mercuric chloride, only slowly deposits a white micro-crystalline compound. If, however, mercuric acetate is used, the absorption of the mixture of butylenes is rapid, and the solution becomes intense red, the addition of potassium hydroxide only precipitating a little mercuric oxide. Potassium chloride is added, the solution allowed to stand for twenty-four hours, and treated with carbon dioxide. In the case of the bromide, the compound is precipitated at this stage, but to obtain the chloride the solution is extracted with ether, from which this salt crystallises. It melts at 52° C., and is easily soluble in alcohol, ether, water, or benzene. The *bromide* crystallises in glistening prisms, M.pt. 66° C., the ether solution forming a compound with ammonia having the composition $HO.C_4H_8.HgBr.NH_3$.

Butene mercuric iodide, C_4H_7HgI.—When potassium iodide is used in the above preparation, Sand and Hofmann state that a butanol compound is not obtained, but the butene derivative. It crystallises in spears from ether, and prisms from benzene or carbon disulphide. All the above substances with 20 per cent. hydrochloric acid give a quantitative yield of olefine and mercuric salt.

When isobutylene is passed into neutral mercuric sulphate solution, it gives an intensely yellow powder of complex composition. This is insoluble in 10 per cent. sulphuric acid, and on boiling with sodium chloride a mixture of calomel and a red chloride, $C_4Cl_4Hg_4(OH)_6,H_2O$, is obtained.

Mercury trichloroethylene, $Hg(CCl{=}CCl_2)_2$.—Trichloroethylene is shaken for several days with an alkaline solution of mercuric cyanide. An oil separates out, the excess of trichloroethylene is removed by evaporation, and the residue recrystallised from ether. It crystallises in colourless, strongly refracting plates, melting at 83° C., easily soluble in alcohol or ether. It is decomposed by yellow ammonium sulphide, mercuric sulphide separating out.

[1] Sand and Hofmann, *loc. cit.*

MERCURY COMPOUNDS DERIVED FROM ACETYLENES.

Products from Mercuric Chloride.—When pure acetylene is passed into mercuric chloride solution a white precipitate is obtained, to which Hofmann [1] gave the structure :

$$(ClHg)_2C{-}CCl_2$$
$$\diagdown\ \diagup$$
$$Hg$$

Biltz and Mumm [2] state that this compound is really a *trichloromercuri-acetaldehyde*, $C(HgCl)_3.CHO$. The evidence put forward is that the analysis corresponds to this formula, and also that the following equation may represent the reaction :

$$C_2H_2+3HgCl_2+H_2O=C(HgCl)_3.CHO+3HCl$$

The equation is based on the fact that the compound when boiled with hydrochloric acid yields 3 mols. of hydrogen chloride and acetaldehyde. Chlorine water converts it into mercuric chloride and chloral :

$$C(HgCl)_3CHO+3Cl_2=CCl_3.CHO+3HgCl_2$$

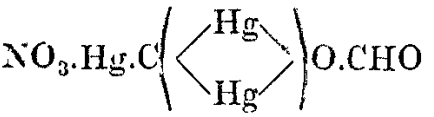
With an aqueous suspension or a potassium iodide solution of iodine, only mercuric iodide is isolated. Permanganate in the presence of sulphuric acid converts it directly to carbon dioxide and mercuric salts, whereas Hofmann stated that trichloromercuri acetic acid was formed. Later,[3] Hofmann admitted that his compound was so rapidly hydrolysed by water that he could not obtain a preparation free from oxygen. He therefore considered his compound to be an aldehyde. When heated with aqueous potassium cyanide, trichloromercuri acetaldehyde yields aldehyde resin, mercuric cyanide, and metallic mercury. No precipitate is formed when acetylene is passed through an aqueous solution of mercuric chloride containing an excess of sodium chloride.

Manchot [4] considers that this trichloromercuri acetaldehyde is merely an additive product of vinyl alcohol.

Although not obtained by the direct action of ethylene, a body to which an ethylenic structure has been assigned is obtained when diethyl ether is shaken with mercury oxychloride. It has been styled *vinyl oxymercurochloride*, $CH_2{=}CH.OHg.O.Hg_2Cl_2$.[5] If boiled for a long time with potassium hydroxide solution, and the residue in alkaline solution treated with nitric acid, a colourless compound is precipitated, $CH{\equiv}C.Hg_2(OH)_2.Hg_2(OH)_2$. It will be noted that the compound has assumed an acetylenic structure, and has been named "*acetylenemercury*." Treated with glacial acetic acid it yields a crystalline *acetate*, $CH{\equiv}C.Hg_2.(OAc)_2.Hg(OAc)_2$, decomposing at 100° C. or when boiled with water. When nitric acid is added to an alkaline solution of vinyl oxymercurochloride, colourless *acetylenemercury oxychloride* is precipitated, $CH{\equiv}C.HgO.HgCl_2$. It is an amorphous powder, insoluble in nitric or hydrochloric acids, ammonium hydroxide, or alkali carbonates, but readily soluble in potassium hydroxide. It is not explosive, but when heated volatilises, leaving a carbon residue.

[1] Hofmann, *Ber.*, 1899, **32**, 870.
[2] Biltz and Mumm, *Ber.*, 1904, **37**, 4417.
[3] Hofmann, *Ber.*, 1904, **37**, 4459.
[4] Manchot, *Annalen*, 1918, **417**, 93.
[5] Poleck and Thümmel, *Ber.*, 1899, **22**, 2863.

From Mercuric Nitrate.[1]—By passing acetylene into a cold solution of mercuric nitrate for fifteen to twenty minutes, Hofmann obtained a *compound* to which he assigned the formula, $C_2Hg_2NO_4H$. He also mentions a compound, $C_2Hg_3NO_5H$, to which he ascribed the constitution,



as being prepared in the following manner: 20 grams of yellow mercuric oxide in 70 c.c. of 30 per cent. nitric acid and 500 c.c. of water is treated with acetylene for two hours at 18° C. A greyish-white, powdery precipitate is obtained. This is mixed with 150 c.c. of 8 per cent. nitric acid, and allowed to stand for six hours at room temperature, and after repeating the operation three times the product is filtered, washed with alcohol and ether, and dried *in vacuo*. If acetylene be passed into hot mercuric nitrate, some mercury separates as well as the above product.

When boiling mercuric nitrate solution is saturated with acetylene the composition of the precipitate is $HgC{\equiv}CHg.HgNO_3.H_2O$. This yields acetaldehyde when treated with dilute acids.

If the mercuric nitrate solution contains an excess of potassium nitrite and 1 per cent. nitric acid and acetylene be passed into the cold mixture, *nitrito-dimercuracetaldehyde* is precipitated as a bright yellow powder. It is explosive, and is proved to be a nitrite by its behaviour towards α-naphthylamine in the presence of acetic and hydrochloric acids.[2]

From Mercuric Oxide.[3]—When acetylene is passed through a suspension of mercuric oxide in boiling phosphoric acid, density 1·15, or in 30 per cent. sulphuric acid, acetaldehyde is produced.

From Mercuric Chlorate and Perchlorate.[4]—*Chloratotrimercuriacetaldehyde*, $ClO_3.Hg.C(Hg_2O).CHO$, is obtained by passing acetylene into an aqueous solution of mercuric chlorate or a mixture of sodium chlorate and mercuric nitrate. The precipitate obtained is digested with 3 per cent. hydrochloric acid. The compound is less explosive than chloratodimercuracetaldehyde. If the perchlorate is substituted for the chlorate, *perchloratomercuracetaldehyde* is formed, the substance being less sensitive to shock than the chlorate.

From Mercuric Bromide.[5]—When acetylene is left in contact with the bromide and water at 100° C. in a sealed flask acetaldehyde is formed, and methyl acetylene under similar conditions yields acetone.

Methyl Acetylene.[6]—When methyl acetylene (allylene) is passed into mercuric chloride solution at ordinary temperatures, a white, crystalline precipitate is obtained. Kutscheroff gave its constitution as $3HgCl_2.3HgO.2C_3H_4$, whilst Biltz and Mumm consider it to be a *trichloromercuri acetone*, $CH_3.CO.C(HgCl)_3$. The product is insoluble in water or cold alcohol, but is decomposed by acids, with the formation of acetone and mercuric salts. The reaction between methyl acetylene

[1] Hofmann, *Ber.*, 1898, 31, 2212, 2783; Erdmann and Köthner, *Zeitsch. anorg. Chem.*, 1898, 18, 48; Köthner, *Ber.*, 1898, 31, 2475.
[2] Hofmann, *Ber.*, 1905, 38, 1999.
[3] Erdmann and Köthner, *Zeitsch. anorg. Chem.*, 1898, 18, 48.
[4] Hofmann, *Ber.*, 1905, 38, 1999.
[5] Kutscheroff, *Ber.*, 1881, 14, 1540.
[6] Kutscheroff, *Ber.*, 1884, 17, 13; Biltz and Mumm, *Ber.*, 1904, 37, 4417.

and mercuric bromide takes place to a less extent, and in the case of mercuric iodide no reaction can be perceived.

A *compound*, $Hg(C_3H_3)_2$, is obtained by the action of methyl acetylene on alkaline solutions of mercuric iodide in potassium iodide, or mercuric chloride. It melts at 203° to 204° C. with slight darkening.[1] Methyl acetylene with mercuric sulphate gives a compound which Kutscheroff designates as $HgSO_4.3HgO.3C_3H_4.7HgO$, and with mercuric acetate a white amorphous precipitate, $HgAc.3HgO.2C_3H_4$.

Ethyl acetylene gives compounds analogous to those from the methyl derivative. They dissolve readily in hydrochloric acid, yielding methyl ethyl ketone, and Biltz and Mumm consider the compound from mercuric chloride to be *trichloromercuri-methyl ethyl ketone*. The compound from alkaline mercuric iodide forms long white needles, M.pt. 162° to 163° C. from 95 per cent. alcohol. *Ethyl n-butyl acetylene* and *ethyl propyl acetylene* are said to yield derivatives with mercuric chloride, but the compounds have not been analysed.[2] The melting-points of the *compounds* obtained from other mono-substituted acetylenes by the action of alkaline mercuric iodide are as follows: *tert.-butylacetylene*, M.pt. 91° to 92° C.; *n-amylacetylene*, M.pt. 61° C.; *n-octylacetylene*, M.pt. 83° to 84° C.[3]

Mercury chloroacetylide, $Hg(C{\equiv}CCl)_2$.[4]—This compound is formed: (1) By shaking sym.-dichloroethylene with mercuric cyanide and aqueous potassium hydroxide solution; (2) the gas obtained by heating trichloroethylene with alcoholic potassium hydroxide is washed with water and concentrated sulphuric acid, then passed into an alkaline mercuric cyanide solution. The product is obtained as a white precipitate, which crystallises from ether in thin quadratic plates, M.pt. 185° C., decomposing with explosion at 195° C. It is not attacked by concentrated hydrochloric acid, but with an ethereal solution of iodine, when exposed to sunlight, it yields chloro tri-iodoethylene, $CCl{\equiv}CI_2$.

Mercury bromoacetylide is prepared as above, using dibromoethylene or tribromoethylene. It crystallises in thin, rectangular plates, decomposing at 153° to 155° C., readily detonating when rubbed on a tile. It is decomposed by boiling with potassium cyanide solution or dilute hydrochloric acid, yielding bromoacetylene, and is volatile in steam. With mercuric bromide it forms an addition compound.

When a mixture of hydrogen and monochloroacetylene is passed into a saturated aqueous solution of mercuric chloride, *trichloromercuri-acetic acid*, $C(HgCl)_3.CO_2H$, is precipitated as a crystalline powder. This is decomposed by hydrochloric acid, yielding acetic acid and mercuric chloride, but in cold potassium hydroxide solution a polymerised form of the acid is obtained. When the mercuric chloride solution contains sodium acetate, chloroacetylene gives *dichloromonohydroxy-trimercuri-acetic acid*, $HgOH.C(HgCl)_2.CO_2H$. From its solution in potassium hydroxide, carbon dioxide precipitates *trihydroxymercuri-acetic acid*,

$$C(HgOH)_3.CO_2H.$$

[1] Johnson and M'Ewen, *J. Amer. Chem. Soc.*, 1926, 48, 472.
[2] Béhal, *Bull. Soc. chim.*, 1888, [2], 49, 581; *Ann. Chim. Phys.*, 1888, [6], 15, 415.
[3] Johnson and M'Ewen, *loc. cit.*
[4] Hofmann and Kirmreuther, *Ber.*, 1908, 41, 314; 1909, 42, 4232.

Products from Phenylacetylene.[1]

From Mercuric Chloride.—A white, insoluble, amorphous solid is obtained. This when boiled with hydrochloric acid and steam distilled yields acetophenone, but if steam distilled after addition of the acid some phenylacetylene is also obtained.

From Mercuric Bromide.—In this case a yellow, crystalline substance is formed, which yields phenylacetylene and acetophenone if treated with concentrated hydrochloric acid and steam distilled.

Mercury phenyl acetylide, $Hg(C_6H_5.C{\equiv}C)_2$, is formed when mercuric oxide reacts with phenylacetylene. This compound has been more recently obtained[2] by dropping a solution of 1 equivalent of phenylacetylene in 20 volumes of 95 per cent. alcohol into a cooled, dilute solution of 2 equivalents of alkaline mercuric iodide, the mixture being mechanically stirred. The product separates as a white, crystalline precipitate if the acetylene solution is not added too rapidly; in the latter case the product is at first sticky, but becomes crystalline on standing. The alkaline mercuric iodide is prepared as follows: 66 grams of mercuric chloride are dissolved in a solution of 163 grams of potassium iodide in 163 c.c. of water, and 125 c.c. of 10 per cent. aq. sodium hydroxide added. The above crystalline precipitate is stirred for two or three minutes, then filtered and washed with 50 per cent. alcohol. The mixture should not be allowed to stand too long before filtration, or secondary reactions set in. The crude product is recrystallised from benzene or 95 per cent. alcohol. From the latter it forms glittering white leaflets, M.pt. 124·5° to 125° C. It is moderately soluble in cold ether or alcohol, readily soluble in chloroform, benzene, or hot alcohol.

The following substituted acetylenes are prepared in a similar manner:—

Mercury benzyl acetylide is purified by solution in hot benzene and precipitation by petroleum ether, then crystallisation from hot, absolute alcohol. It forms white needles, M.pt. 106·5° to 107·5° C.

Mercury phenyl ethyl acetylide occurs as small, white crystals, M.pt. 83·5° to 84·5° C.

Mercury p-tolyl acetylide yields long, white needles, M.pt. 199° to 202° C.; yield 75 per cent. It is moderately soluble in warm benzene or toluene, slightly soluble in cold, sparingly soluble in ether or boiling alcohol, and almost insoluble in cold alcohol.

Mercury p-anisyl acetylide forms small, white crystals from toluene, M.pt. 207° to 209° C., when rapidly heated. When heated slowly, the salt turns brown before the melting-point is reached.

Mercury hexahydrobenzyl acetylide yields long, white needles, M.pt. 104° C.; yield 78 per cent.

Mercury phenoxymethyl acetylide gives long, white needles, M.pt. 120·5° to 121° C.; yield 84 per cent.

Mercury tribromoethylene.—Acetylene tetrabromide is shaken for about ten hours with alkaline mercuric cyanide solution. A crystalline deposit is obtained, which after crystallisation from ether yields monoclinic prisms, the parameters of which are $a : b : c = 1{\cdot}4829 : 1 : 0{\cdot}5637$; $\beta = 105°\ 26'$, M.pt. 141° C. With yellow ammonium sulphide

[1] Manchot and Haas, *Annalen*, 1913, 399, 123; Biltz and Reinkober, *Annalen*, 1914, 404, 219; Nef, *Annalen*, 1899, 308, 299.

[2] Johnson and M'Ewen, *J. Amer. Chem. Soc.*, 1926, 48, 472.

it gives tribromoethylene, but is not decomposed by boiling water or 10 per cent. hydrochloric acid.[1]

Vinyl bromide[2] (monobromoethylene) gives a white, amorphous compound when heated with mercuric acetate at 100° C., the product probably being a compound of acetaldehyde with mercurous bromide.

Mercuration of Styrol (phenylethylene).[3]—Two grams of styrol with a solution of 19 grams of mercuric acetate in 170 c.c. of water are shaken for eight hours and the reaction product poured into 10 per cent. sodium chloride solution. The product is easily decomposed, and with sodium hydroxide becomes yellow, with ammonium sulphide black. It crystallises from water in plates, M.pt. 112° C., the aqueous solution having an odour of styrol, which becomes intense on warming. A similar product is obtained if a mixture of mercuric chloride and acetate is used. The composition is given as $3C_8H_8.3HgOHCl.HgCl_2$.

When styryl ethyl ether is warmed at 50° C. with an aqueous solution containing 3 mols. of mercuric acetate, and poured after two hours into 10 per cent. sodium chloride, a white precipitate is obtained.[4] The substance formulated as CHPh=CH.OH,2HgClOH, partially melts about 120° C., is stable towards dilute acids, but decomposed by hydrochloric acid, yielding phenylacetaldehyde.

DERIVATIVES OF CYCLO- AND DICYCLO-PENTADIENE.[5]

Cyclopentadiene when shaken with an alcoholic solution of mercuric chloride and sodium acetate gives a heavy white precipitate of **dichloromercuri cyclopentadiene**, $C_5H_4(HgCl)_2$, insoluble in all solvents.

Chloromercuri methoxy dicyclopentadiene.—To 35 grams of mercuric chloride in 200 c.c. of acetone-free methyl alcohol, 5 c.c. of dicyclopentadiene are added, and the mixture allowed to stand for two days at 15° C. It is then filtered, and the filtrate added to boiling water until turbidity disappears, and on cooling the compound is deposited in shining crystals. Yield 10 to 12 grams. It is obtained in pale yellow needles, M.pt. 133° C., when recrystallised from aqueous methyl alcohol (1 : 2). In alcohols, ether, acetone, benzene, or acetic acid it is readily soluble, also in hot alkali. Boiling potassium cyanide solution or acids convert it into dicyclopentadiene and mercuric salts. When its solution in concentrated sulphuric acid is warmed it assumes a pink coloration, with a green fluorescence.

If the methyl alcohol in the above preparation is replaced by ethyl alcohol, the corresponding *ethoxy compound* is formed. It crystallises from aqueous alcohol in prisms, M.pt. 98° C.

The *amyloxy compound* is a heavy oil, which solidifies at −12° C., and is soluble in hot methyl alcohol, from which solution it may be precipitated by the addition of water.

ALKYL AND ARYL MERCURIC ALKYL XANTHATES.[6]

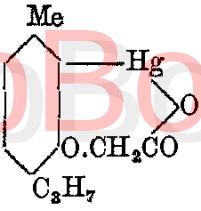
To the alcoholic solutions of the alkyl or aryl mercuric hydroxides, obtained from the corresponding chlorides by treatment with sodium

[1] Hofmann and Kirmreuther, *Ber.*, 1908, 41, 314; 1909, 42, 4232.
[2] Saytzeff and Glinsky, *Jahresber.*, 1867, 563; *Zeitsch. Chem.*, 1867, [2], 3, 675; *Bull. Soc. chim.*, 1868, [2], 9, 474.
[3] Manchot, *Annalen*, 1920, 421, 316.
[4] Manchot, Haas, and Mählrlein, *Annalen*, 1918, 417, 93.
[5] Thiele, *Ber.*, 1901, 34, 71; Hofmann and Seiler, *Ber.*, 1906, 39, 3187.
[6] Koten and Adams, *J. Amer. Chem. Soc.*, 1924, 46, 2767.

hydroxide in 200 c.c. of absolute alcohol, 15 c.c. of carbon disulphide are added. A slight evolution of heat is noticed, and a faint yellow colour develops. Partial evaporation at room temperature precipitates the compounds, which are recrystallised from 95 per cent. alcohol. The products are white, and the yields average 70 per cent. They are soluble in ether, chloroform, or hot alcohol, but insoluble in water. Exposure to sunlight causes them to blacken. Iodine in chloroform solution decomposes the compounds, forming the corresponding alkyl or aryl iodides and a yellow oil. The following substances have been obtained: *methylmercuric methyl xanthate*, $CH_3O-CS-SHgCH_3$, M.pt. 59° C.; *methylmercuric ethyl xanthate*, M.pt. 69° C.; *ethylmercuric ethyl xanthate*, M.pt. 53° C.; *n-propylmercuric ethyl xanthate*, M.pt. 38° to 39° C.; *n-butylmercuric ethyl xanthate*, oil; *p-tolylmercuric ethyl xanthate*, M.pt. 128° C.: *p-tolylmercuric methyl xanthate*, M.pt. 145° C.; *benzylmercuric ethyl xanthate*, M.pt. 74° C.

DERIVATIVES OF SUBSTITUTED ARYLOXY-FATTY ACIDS.[1]

From Thymoxy-acetic Acid.—One hundred parts of the acid are suspended in 2500 parts of water and mixed with a solution of 160 parts of mercuric acetate. After warming for one hour at 70° to 80° C. an insoluble sandy powder separates. It is purified by solution in strong alkali and precipitation by carbon dioxide. It is insoluble in the usual organic solvents, but readily soluble in alkali. The mercury is split off again when heated with dilute hydrochloric acid. The compound has the following constitution :—



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In the same way the following acids may be mercurated: *α-guiacol-propionic acid*, *α-cravoxy-propionic acid*, *o-chlorophenylglycollic acid*, *naphthol fatty acids* or *salicyloxy-acetic-acid* or their derivatives.[2]

DERIVATIVES OF HYDRAZINES.[3]

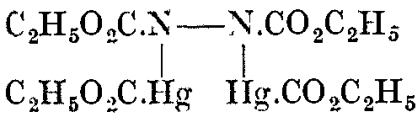
A solution of 30 grams of ethyl hydrazinecarboxylate in 150 c.c. of water is added to 63 grams of freshly precipitated mercuric oxide suspended in 1 litre of water. A violent gas evolution soon takes place and heat is developed. The yellow colour of the mercuric oxide disappears, and the mass becomes dirty green. After the reaction subsides, the whole is left for several hours, then boiled and filtered. The residue is boiled up several times, with about 500 c.c. of water, and from the filtrate colourless needles separate on cooling. These are recrystallised from much water or a little benzene

[1] German Patent, 261229; *cf.* American Patent, 1074781; British Patent, 4075 (1913).

[2] German Patent, 264267, deals with the combination of the above type of derivative from phenoxyacetic acid with alanine to form a water-soluble double compound. The compound of o-chlorphenoxyacetic acid is combined with sodium diethylbarbiturate. The mercury compounds may be replaced by the derivatives of pyrocatechol glycollic acid, p-cresoxyvalerianic acid or xylenol butyric acid, and the alanine and sodium diethyl barbiturate by urea, acid amides or imides, caffeine or polypeptides; *cf.* German Patent, 261875.

[3] Diels and Uthemann, *Ber.*, 1920, 53, [B.] 723.

or toluene. Yield 5 grams. The compound melts at 155° C. and has the following constitution :—

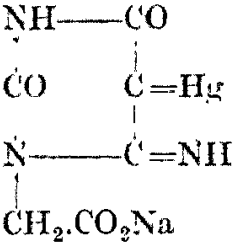


It is decomposed by hydrochloric acid into ethyl hydrazodicarboxylate, mercuric chloride, carbon monoxide, and alcohol ; by piperidine into ethyl hydrazodicarboxylate, mercury, and piperylurethane ; by bromine into ethyl azodicarboxylate, mercuric bromide, and ethyl bromoformate.

A similar derivative is formed from methyl hydrazine carboxylate. It melts at 215° C. and has similar properties to the ethyl compound.

DERIVATIVE OF PYRIMIDINE.[1]

Sixty parts of freshly precipitated mercuric oxide and 50 parts of 2 : 6-dihydroxy-4-imino-dihydropyrimidine-3-acetic acid (sodium salt) in 200 parts of water are shaken for ten hours. The greater part of the mercuric oxide dissolves. The filtrate is concentrated *in vacuo* and the residue treated with pure alcohol, the mercury derivative being precipitated pure in a crystalline form. It is extremely soluble in water, alkalies, or carbonates, insoluble in alcohol, ether, chloroform, or benzene. The compound has the constitution :[2]



DERIVATIVES OF SALICYL AND NITROSALICYLALDEHYDES.[3]

3 : 5-Diacetoxymercuri salicylaldehyde.—Ten grams of the aldehyde and 32 grams of mercuric acetate are dissolved in 500 c.c. of 50 per cent. alcohol containing 5 c.c. of acetic acid, and heated for one hour at 100° C. From the cold, filtered solution 32 grams of crude diacetate are obtained, the filtrate yielding a further 10 grams if left overnight. The addition of sodium chloride to the filtrate gives 8 grams of dichloro compound.

The diacetate is soluble in acetic acid, but insoluble in other solvents. It crystallises in needles, M.pt. 234° C. with decomposition. It is soluble in aqueous sodium hydroxide, and when boiled with alcoholic potassium iodide the mercury is split off and salicylaldehyde and potassium hydroxide formed. With hydroxylamine or phenylhydrazine, metallic mercury is precipitated.

The above dichloro compound is insoluble in organic solvents and does not melt at 270° C.

[1] German Patent, 224491.

[2] For derivatives of pyramidone, see Weehuizen, *Chem. Zentr.*, 1906, ii. 1628 ; Oliveri-Mandalà, *Gazzetta*, 1921, 51, i. 125.

[3] Whitmore and Middleton, *J. Amer. Chem. Soc.*, 1923, 45, 1330 ; Henry and Sharp, *Trans. Chem. Soc.*, 1922, 121, 1055.

3(?)-Chloromercuri salicylaldehyde.—Ten grams of aldehyde in 2 litres of water are treated with 26 grams of mercuric acetate, and the mixture mechanically stirred until no mercury ions can be detected in a test portion after filtering. Filtration yields 3 grams of diacetate, and sodium chloride precipitates 19 grams of a mixture of mono and dichloro compound from the filtrate. Repeated extraction with boiling alcohol gives 5 grams of pure monochloromercuri salicylaldehyde. M.pt. 189° to 190° C. When this is suspended in chloroform and treated with one molecular proportion of iodine, an iodosalicylaldehyde, M.pt. 52° to 58° C., is isolated, 3-iodosalicylaldehyde melting at 55° C.

3-Acetoxymercuri-5-nitrosalicylaldehyde.—Twelve grams of the aldehyde and 23 grams of mercuric acetate in 400 c.c. of alcohol and 5 c.c. of acetic acid are heated for one hour at 100° C. Filtration gives 26 grams of product, which deposits pale yellow crystals from acetic acid, which do not melt at 260° C. Its solution in sodium hydroxide is yellow, and when acidified with hydrochloric acid gives the corresponding *chloride*. This is insoluble in organic solvents and does not melt at 260° C.

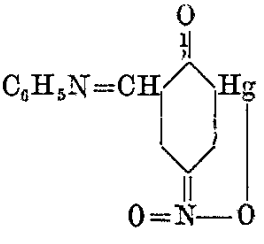
5-Acetoxymercuri-3-nitrosalicylaldehyde.—Four grams of aldehyde and 7 grams of mercuric acetate when treated as above give 9 grams of the compound. It is insoluble in organic solvents and does not melt at 260° C.

Condensation of the foregoing Mercurated Salicylaldehydes with Aromatic Amines.

2 : 5-Diacetoxymercuri salicylal aniline.—Five grams of the diacetate in 10 c.c. of hot aniline give 5·5 grams of a brick-red, amorphous product, insoluble in organic solvents and not melting at 260° C. A similar product is obtained from p-toluidine. *p-Aminobenzoic acid* gives a deep red, insoluble powder, and *anthranilic acid* a similar compound.

3(?)-Chloromercuri salicylal aniline yields flat, yellow plates, M.pt. 182° to 184° C., insoluble in organic solvents.

3-Hydroxymercuri-5-nitrosalicylal aniline anhydride,



is obtained by condensation between 3-acetoxymercuri-5-nitrosalicyl aldehyde and aniline, 1 mol. of acetic acid being lost during the condensation or on drying. It is a red, amorphous product, insoluble in organic solvents, but soluble in alkali.

3-Chloromercuri-5-nitrosalicylal aniline is an orange-red compound.

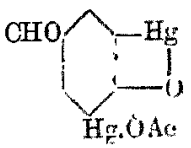
DERIVATIVES OF META AND P-HYDROXYBENZALDEHYDES AND THEIR NITRO COMPOUNDS.[1]

2-Acetoxymercuri-3-hydroxybenzaldehyde, $AcO.Hg.C_6H_3(OH).CHO$.—One molecular proportion of the aldehyde in 50 per cent. alcohol is mixed with one molecular proportion of mercuric acetate

[1] Henry and Sharp, *Trans. Chem. Soc.*, 1922, 121, 1056.

in 50 per cent. alcohol containing 1 per cent. of acetic acid. The mixture is boiled under reflux and the reaction mixture concentrated, when a precipitate separates. This is filtered off, washed with water, alcohol, and ether, and dried. Recrystallisation from alcohol containing 5 per cent. of acetic acid gives colourless needles, M.pt. 185° to 186° C. (corr.) with decomposition. It is soluble in sodium hydroxide, and is coloured yellow by sulphuric acid. Iodine in potassium iodide solution converts it into iodo-m-hydroxybenzaldehyde, and potassium permanganate in acetone solution oxidises it to an iodo-m-hydroxybenzoic acid. Potassium nitrate in sulphuric acid below 0° C. gives 2-nitro-3-hydroxybenzaldehyde.

4 : 5 - Anhydro - 3 - acetoxymercuri - 5 - hydroxymercuri-4-hydroxybenzaldehyde,



When the preceding method is applied to p-hydroxybenzaldehyde, this anhydro derivative is produced. It is a colourless, crystalline powder, insoluble in water and most organic solvents, and has no melting point. It is soluble in hot acetic acid, being converted into 3 : 5-*diacetoxydimercuri-4-hydroxybenzaldehyde*, minute, colourless, glistening plates being deposited as the solution cools. This compound darkens on heating, but does not melt below 300° C. The diacetoxy derivative gives a turbid solution in sodium hydroxide, from which carbon dioxide precipitates 3 : 5-*dihydroxydimercuri-4-hydroxybenzaldehyde*, and with hydrochloric acid the *dichlorodimercuri* compound is obtained.

Iodine in potassium iodide solution converts the anhydro compound into 3 : 5-di-iodo-4-hydroxybenzaldehyde.

The following method of preparation is a general one for the compounds now described. The nitrohydroxybenzaldehyde (1 mol.) with mercuric acetate (1 mol. or 2 mols.) in 50 per cent. alcohol containing a little acetic acid is boiled until a test portion is completely soluble in sodium hydroxide.[1]

5-Hydroxymercuri-3-nitro-4-hydroxybenzaldehyde occurs as microscopic, orange platelets, darkening about 285° C., but not melting at 300° C. It forms an orange solution in sodium hydroxide. Addition of hydrochloric acid to this solution precipitates the *chloromercuri compound*, which crystallises from alcohol in tufts of minute, colourless needles, M.pt. 226° C. (corr.) with decomposition. From a solution of the hydroxymercuri compound in glacial acetic acid the *acetoxymercuri derivative* separates in colourless prisms, darkening about 250° C., but not melting at 300° C. The hydroxymercuri compound, when shaken with an excess of 5 per cent. solution of iodine in potassium iodide, is converted quantitatively into iodo-3-nitro-4-hydroxybenzaldehyde.

The mercuration of 6-nitro-3-hydroxybenzaldehyde leads to the production of a solid (A) consisting of dimercurated compounds, and concentration of the filtrate from this yields mixtures of mono- and dimercurated compounds.

Products from A.—This product proves to be insoluble in the usual

[1] Henry and Sharp, *Trans. Chem. Soc.*, 1924, 125, 1049.

solvents, but dissolves in formic, acetic, propionic, or n-butyric acids. From propionic acid, orange-yellow needles of **2 : 4-dipropionoxy-dimercuri-6-nitro-3-hydroxybenzaldehyde** separate. These explode at 235° C. (corr.) and are sparingly soluble in sodium hydroxide, to which they impart an orange colour. If hydrochloric acid is added to this solution, the 2 : 4-*dichlorodimercuri* compound is precipitated, and may be recrystallised from alcohol in colourless, microscopic needles.

The monomercurated compound is obtained from the more soluble fractions by extraction with ether, dissolving the residue in potassium hydroxide solution and adding hydrochloric acid. **Monochloro-mercuri-6-nitro-3-hydroxybenzaldehyde** is thus precipitated. It decomposes at 198° C. (corr.). The dimercurated product is converted by 5 per cent. bromine in alcohol into 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde, and with iodine in potassium iodide solution into 2 : 4-diiodo-6-nitro-3-hydroxybenzaldehyde. The monomercuri compound in a similar manner yields monoiodo-6-nitro-3-hydroxybenzaldehyde.

If two molecular proportions of mercuric acetate be used, most of the product consists of dimercurated compounds.

4-Nitro-3-hydroxybenzaldehyde also yields a mixture of compounds. The dimercurated product appears to be a **hydroxymercuri-acetoxy-mercuri-4-nitro-3-hydroxybenzaldehyde**. It is insoluble in most solvents, but gives 2 : 6-*diformoxydimercuri-4-nitro-3-hydroxybenzaldehyde* from hot formic acid solution. It crystallises in pale yellow needles, which darken at 120° C. and explode at 257° C. When boiled with formic acid, metallic mercury separates. It gives a red solution in potassium hydroxide, from which hydrochloric acid precipitates the 2 : 6-*dichloro-dimercuri derivative*. This crystallises from alcohol in bundles of minute, pale yellow needles, which darken at 240° C. but do not melt at 300° C. When heated *in vacuo* it loses a molecule of water at 60° C., and decomposes at 282° C. (corr.). Its potassium hydroxide solution is decomposed by carbon dioxide with precipitation of **2 : 3-anhydro-2 : 6-dihydroxymercuri-4-nitro-3-hydroxybenzaldehyde**. The dimercurated compound may be converted by the usual means into a di-iodo-4-nitro-3-hydroxybenzaldehyde.

Monoformoxymercuri-4-nitro-3-hydroxybenzaldehyde may be obtained from the monomercurated compound. It melts at 233° to 235° C. (corr.) with decomposition. Other compounds from this hydroxybenzaldehyde are: *propionoxymercuri-4-nitro-3-hydroxybenzaldehyde*, pale orange needles; *chloromercuri-4-nitro-3-hydroxybenzaldehyde*, decomposing about 187° C. The monomercuri compounds may be converted to an iodo-4-nitro-3-hydroxybenzaldehyde.

Using the general methods described in the preceding cases, 2-nitro-3-hydroxybenzaldehyde yields the following derivatives: *hydroxy-mercuriacetoxymercuri-2-nitro-3-hydroxybenzaldehyde*, amorphous; *di-acetoxydimercuri-2-nitro-3-hydroxybenzaldehyde*, pale yellow needles; *dichlorodimercuri-2-nitro-3-hydroxybenzaldehyde*, pale green, decomposing at 236° C. (corr.); *acetoxymercuri-2-nitro-3-hydroxybenzaldehyde*, bundles of microscopic needles, not melting at 300° C.; *chloromercuri-2-nitro-3-hydroxybenzaldehyde*, decomposing about 207° C.

Other substituted Benzaldehydes.[1]—**2-Hydroxy-3-acetoxymercuri-5-tert.-butylbenzaldehyde**.—The aldehyde and mercuric acetate in molecular proportions are dissolved in alcohol containing acetic acid

[1] Henry and Sharp, *loc. cit.*

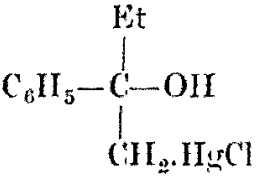
and boiled for fifteen minutes. The hot solution is then poured into a large volume of water, the resulting white precipitate filtered off immediately and dried *in vacuo*. Recrystallisation from alcohol containing acetic acid gives white, needle-shaped crystals, M.pt. 220° C. If the above preparation be repeated without using a solvent and the mixture heated for two hours on the water-bath, a 73 per cent. yield is obtained.

2-Hydroxy-3-acetoxymercuri-5-isoamylbenzaldehyde. This compound is prepared by the second method mentioned above. It crystallises in bundles of white needles, M.pt. 134° to 135° C.

DERIVATIVES OF ACETOPHENONE.[1]

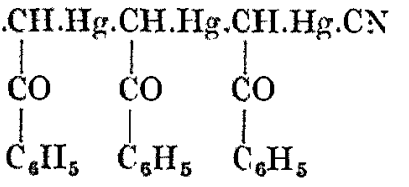
Phenacylmercuric chloride, $C_6H_5.CO.CH_2.HgCl$. Two parts of mercuric acetate and three parts of acetophenone are quickly heated in an oil-bath to 150° C., and the temperature maintained until mercury ions can no longer be detected. The mixture is filtered hot and treated with an excess of aqueous sodium chloride. The precipitate is extracted with ether to remove the excess of acetophenone and recrystallised from high-boiling ligroin. Needles are obtained, M.pt. 145° to 146° C. Warmed with dilute hydrochloric acid it gives acetophenone and mercuric chloride; and with cold ammonium sulphide, acetophenone and mercuric sulphide. Bromine yields phenacyl bromide.

It reacts violently with ethyl magnesium bromide forming (*chloromercuri methyl*)-*ethyl-phenyl-carbinol*,



This is a crystalline powder, M.pt. 129° to 131° C. with decomposition, ammonium sulphide decomposing it with the formation of mercuric sulphide.

Acetophenone yields a precipitate when added to an aqueous solution containing mercuric cyanide and sodium hydroxide. It is a pale yellow, insoluble powder, which retains about 3 per cent. of water when dried in air. Like the acetone compound, it is decomposed by potassium cyanide or hydrochloric acid. Its constitution may be expressed as $3(C_6H_5.CO.CH{=}Hg)$, HgC_2N_2 or



Diphenylmethyl ketone also gives a compound with mercuric cyanide in alkaline solution.

Products from Benzalacetophenone.[2]—**α-Acetoxymercuri-β-methoxy-β-phenylpropiophenone.**—A solution of 25 grams of benzalaceto-

[1] Dimroth, *Ber.*, 1902, 35, 2853; Marsh and Fleming Struthers, *Trans. Chem. Soc.*, 1905, 87, 1881; Grignard and Abelmann, *Bull. Soc. chim.*, 1916, [iv.], 19, 18.

[2] Middleton, *J. Amer. Chem. Soc.*, 1923, 54, 2763.

phenone and 38 grams of mercuric acetate in 250 c.c. of absolute methyl alcohol is allowed to stand until a sample is soluble in sodium hydroxide. The solution yields 53 grams of product on evaporation, and when recrystallised from methyl alcohol it melts at 115° C. When treated with potassium bromide (1 mol.) in alcoholic solution it yields the *α-bromomercuri* derivative, M.pt. 141° C., but with one molecular equivalent of bromine the mercury is split off, and α-bromo-β-methoxy-β-phenylpropiophenone is formed. The latter compound when treated with sodium methylate and afterwards with mercuric acetate yields the diacetoxymercuri derivative of dibenzoyl methane. The above α-bromomercuri compound reacts with ethyl magnesium bromide, giving β-phenyl valerophenone and mercury diethyl. The α-acetoxymercuri derivative is slowly decomposed by cold hydrochlorie acid, and rapidly by hot acid, mercuric chloride and benzalacetophenone being formed. Hydrogen sulphide gives an immediate precipitate of mercuric sulphide when passed through an alcoholic solution of the compound, and an aqueous solution of potassium iodide on boiling decomposes the compound with the formation of benzalacetophenone.

In a similar manner the following compounds may be prepared, and have properties like those of the above compounds:—

α-Acetoxymercuri-β-ethoxy-β-phenyl propiophenone is formed as above, but using ethyl instead of methyl alcohol in the preparation. It melts at 134° C.

The *α-bromomercuri* compound melts at 138° C., and *α-acetoxymercuri-β-methoxy-β-phenyl-p-chloropropiophenone* has M.pt. 124° C. Dibenzalacetone yields an *acetoxymercurimethoxy* derivative, M.pt. 183° C.; and an *ethoxy* compound, M.pt. 188° to 190° C.

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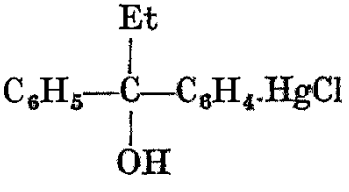
DERIVATIVES OF BENZOPHENONE.[1]

o-Chloromercuri benzophenone.—Dry mercuric acetate is heated with an excess of benzophenone (3 mols.) in an oil-bath at 120° C. and finally at 130° C. until the reaction is complete. The mixture is poured into a hot salt solution and shaken with ether. The latter is distilled off and the benzophenone removed by ligroin, a mixture of mono and dimercurated compounds remaining. Recrystallisation from alcohol produces glittering plates of the mono derivative, M.pt. 167° to 168° C. Yield 40 per cent. It is readily soluble in acetone, chloroform, or ethyl acetate, sparingly in ligroin. It is decomposed by boiling hydrochloric acid into benzophenone and mercuric chloride, and its warm solutions are slowly decomposed by hydrogen sulphide. With magnesium ethyl bromide it forms *phenyl o-chloromercuriphenyl ethyl carbinol*, which may be crystallised from ether-ligroin, M.pt. 106° C. with decomposition. It reacts vigorously with Grignard reagents, but gives no reaction in the cold with hydrogen or ammonium sulphides, owing to the attachment of the mercury to the nucleus, as shown :



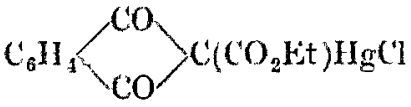
[1] Dimroth, *Ber.*, 1902, 35, 2853; Grignard and Abelmann, *Bull. Soc. chim.*, 1916, [iv.], 19, 18.

The *dichloromercuri* compound crystallises from hot alcohol as a yellow powder.

o-Bromomercuri benzophenone is prepared in a similar manner to the chloride. It melts at about 176° C., is difficultly soluble in alcohol or ether, and bromine transforms it to bromobenzophenone. The latter gives o-bromobenzophenone oxime (M.pt. 132° to 133° C.), and this with alkali gives phenyl indoxazene, thus fixing the constitution of the bromo compound.

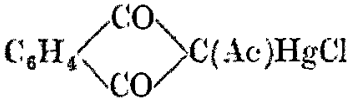
DERIVATIVES OF INDANDIONE AND OXINDONE.

2-Chloromercuri-2-carbethoxy-indandione,[1]



The sodium compound reacts with aqueous mercuric chloride to give the above derivative. It crystallises in colourless prisms, M.pt. 240° to 245° C., and is insoluble in the usual solvents, but dissolves in pyridine.

2-Chloromercuri-2-acetyl-indandione,



The condensation of ethyl phthalate and acetone in the presence of sodium yields 2-acetyl-indandione, and this reacts with mercuric chloride forming a colourless, micro-crystalline powder.

2-Chloromercuri indandione is obtained by treating sodio-1 : 3-diketohydrindene with excess of mercuric chloride in aqueous or alcoholic solution.[2] The pale yellow salt is easily soluble in pyridine, but with difficulty in sodium hydroxide. When shaken for two days with sodium carbonate the colour changes from yellow to white, and the corresponding *hydroxide* is obtained as a white solid.

DERIVATIVES OF CAMPHOR.[3]

αα-Di-iodomercuri camphor.—1. Camphor (9 grams) is dissolved in a solution containing 1·5 grams of potassium in 50 c.c. of absolute alcohol. The addition of 13·5 grams of mercuric iodide gives no precipitate and the solution is poured into water, a white product being deposited. The liquid is saturated with carbon dioxide to prevent reduction, and the precipitate collected and dried. It is digested with aqueous potassium iodide to remove excess of mercuric iodide, washed and dried. Yield 6·5 grams. Reaction is in accordance with the equation :

$$9C_{10}H_{16}O + 4HgI_2 + 2KOC_2H_5 = C_{10}H_{14}OHg_2I_2 + 2KHgI_3, 4C_{10}H_{16}O + 2C_2H_6O$$

2. A solution of 0·75 gram of camphor in a little petroleum is added to a mixture of 50 c.c. of Normal potassium hydroxide and 6·7 grams of

[1] Hantzsch and Gajewski, *Annalen*, 1912, 392, 302.
[2] Peters, *Ber.*, 1907, 40, 235.
[3] Marsh and Fleming Struthers, *Trans. Chem. Soc.*, 1909, 95, 1777; Marsh, *ibid.*, 1910, 97, 1410.

mercuric iodide, and the mixture shaken until the red colour disappears. The petroleum is removed *in vacuo* and the precipitate washed and dried. The above quantities are taken in accordance with the equation :

$$C_{10}H_{16}O+3HgI_2+2KOH=C_{10}H_{14}OHg_2I_2+K_2HgI_4+2H_2O$$

It is found, however, that the product contains a small variable amount of the compound $C_{10}H_{14}O.Hg_2O$.

3. By the action of cold glacial acetic acid on the substance $(C_{10}H_{14}O)_3Hg_4I_2$, a 53 per cent. yield of di-iodide is obtained.

$$(C_{10}H_{14}O)_3Hg_4I_2+2C_2H_4O_2=C_{10}H_{14}OHg_2I_2+2C_{10}H_{15}O.Hg.C_2H_3O_2$$

The di-iodide is a colourless, amorphous powder, insoluble in water and neutral solvents. It sublimes without melting and apparently without decomposition. It is unaffected by aqueous potassium iodide, and is insoluble in alcohol or acetone, but when mixed with potassium iodide it is soluble in both these solvents.

Compound $(C_{10}H_{14}O)_3Hg_4I_2$.—This body is prepared by dissolving camphor in a little petroleum and heating on a water-bath for twenty-four hours with an alkaline solution of potassium mercuric iodide. The precipitate is dried at 100° C. A 51 per cent. yield is obtained using 2 grams of potassium iodide, 21 grams of camphor, and 63 grams of mercuric iodide, the latter being added in thirteen stages.

It is a pale yellow, amorphous powder, scarcely affected by ordinary solvents. Aqueous potassium iodide only slowly decomposes it, but in acetone solution the decomposition is rapid. Halogen acids yield mercuric salt and camphor. Concentrated nitric acid oxidises it to camphoric acid, and concentrated sulphuric acid decomposes it, with separation of mercuric iodide. Cold glacial acetic acid gives di-iodo-mercuri camphor, but hot glacial acetic acid yields *α-acetoxymercuri camphor* only, no di-iodide being formed.

$$C_{10}H_{14}O_3Hg_4I_2+3C_2H_4O_2=HgI+3C_{10}H_{15}O.Hg.C_2H_3O_2$$

With a cold solution of iodine in benzene $(C_{10}H_{14}O)_3Hg_4I_2$ yields di-iodocamphor. Prolonged heating with potassium hydroxide eventually gives a compound represented by $(C_{10}H_{14}O)_2Hg_3O$. Condensation of camphor with mercuric iodide in the presence of alkali probably first forms the di-iodo compound, which on further heating condenses to $(C_{10}H_{14}O)_3Hg_4I_2$. If in the preparation of the latter the amount of potassium iodide is diminished, a compound agreeing with the formula $(C_{10}H_{14}O)_5Hg_6I_2$ is formed. It is likely that the potassium hydroxide and iodine acting on $(C_{10}H_{14}O)_3Hg_4I_2$, first form more highly condensed compounds, $(C_{10}H_{14}O)_4Hg_5I_2$ and $(C_{10}H_{14}O)_5Hg_6I_2$, and the latter is decomposed by potassium hydroxide as follows :—

$$4(C_{10}H_{14}O)_3Hg_4I_2=3(C_{10}H_{14}O)_4Hg_5I_2+HgI_2$$
$$5(C_{10}H_{14}O)_4Hg_5I_2=4(C_{10}H_{14}O)_5Hg_6I_2+HgI_2$$
$$(C_{10}H_{14}O)_5Hg_6I_2+2KOH=2(C_{10}H_{14}O)_2Hg_3O+C_{10}H_{16}O+2KI$$

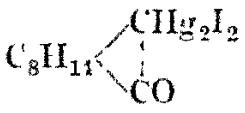
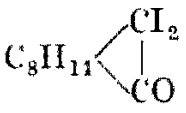
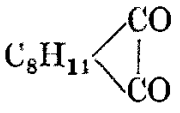
In the series $(C_{10}H_{14}O)_2Hg_3I_2$ is missing, but is probably represented by $(C_{10}H_{14}O)_2Hg_3O$.

α-Chloromercuri camphor, $C_{10}H_{15}O.HgCl$.—The compound $(C_{10}H_{14}O)_3Hg_4I_2$ is dissolved in cold glacial acetic acid and the solution treated with sodium chloride. It crystallises well from glacial acetic

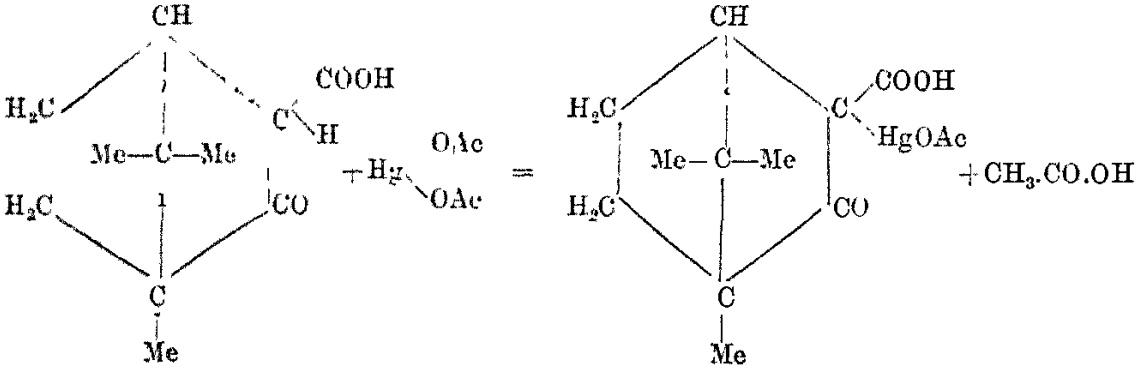
acid, the crystals melting at 222° C., but is insoluble in water. The *bromide* separates from glacial acetic acid in colourless, transparent crystals, M.pt. 220° to 221° C., insoluble in water. Using potassium iodide, the *α-iodomercuri* compound is obtained as a *double salt* with mercuric iodide, $C_{10}H_{15}O.HgI.HgI_2$. The mercuric iodide may be removed by the action of potassium iodide in neutral solution, the α-iodide being left as a nearly colourless precipitate. It crystallises from ethyl acetate in minute, colourless crystals, M.pt. 184° C., decomposed by glacial acetic acid.

α-Mercuri camphor oxide, $(C_{10}H_{15}OHg)_2O$, is obtained from the acetate by treatment with pure potassium hydroxide. It is readily soluble in alcohol or carbon disulphide, evaporation of the latter solution leaving a clear, transparent glassy solid.

In all the above compounds the mercury appears to be in the mercuric state, no mercurous salts having been obtained by decomposition with halogen acids. The structural relationships of the mercury and iodine derivatives to camphor quinone is shown by the formulæ :

Products from Camphorcarboxylic acid.[1]—To a methyl alcohol solution of 98 parts of the acid, a solution of 160 parts of mercuric acetate is added, a precipitate soon separating. After twelve hours the mixture is filtered, the residue washed with alcohol and water, and dried. The product is a snow-white powder. The *carboxylic methyl ester* has been treated in a similar manner. The reaction is represented as follows :—



From Camphene.[2]—A saturated aqueous solution of 2 mols. of mercuric acetate is shaken with a solution of 1 mol. of camphene in petroleum ether for thirty days. White, glistening, colourless plates are obtained, M.pt. 188° to 189° C., having the composition $C_{10}H_{16}O.(Hg.OAc)_2$. Hydrogen sulphide regenerates camphene. The corresponding *chloride* is a white, amorphous powder, insoluble in all neutral solvents. It sinters at 150° C. and does not melt at 250° C. Reduction by sodium amalgam in aqueous solution, or zinc and potassium hydroxide, yields camphene.

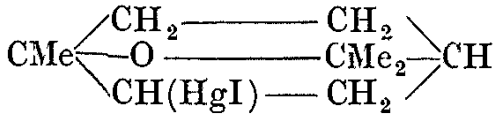
l-Pinene when treated with mercuric acetate yields dioxypinene.[3]

[1] German Patent, 275932.
[2] Balbiano and Paolini, *Ber.*, 1903, 36, 3575.
[3] Balbiano and Paolini, *Ber.*, 1902, 35, 2994 ; *Atti. R. Accad. Lincei*, 1902, [v.], 11, ii. 65.

DERIVATIVES OF TERPINEOL AND DIMETHYLHEPTENOL.[1]

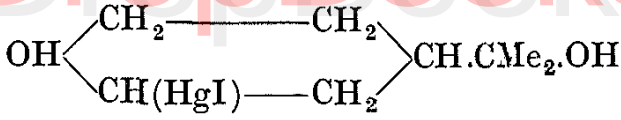
Yellow mercuric oxide is dissolved in 20 per cent. nitric acid, and potassium hydroxide added until the basic nitrate begins to appear. An ethereal solution of terpineol is then added and the mixture shaken until a clear solution is obtained. More potassium hydroxide is added and the precipitate again dissolved by more terpineol, these processes being repeated until the addition of the alkali gives a black precipitate. The solution is then made strongly alkaline, and potassium iodide added, when iodomercuri cineol is at once precipitated. This is filtered off, and from the filtrate in a few days a crop of **α-iodomercuri trans-terpineol** crystallises out. If these crystals are filtered off and carbon dioxide passed through the filtrate, **β-iodomercuri-trans-terpineol** is precipitated.

α-Iodomercuri cineol,



crystallises from alcohol in small, glistening prisms, which dissolve very readily in cold benzene or chloroform. It becomes yellow at 115° C. and melts with decomposition at 152° to 154° C. It does not yield a benzoate, and reduction with sodium amalgam does not give a terpineol, but a mobile oil. This gives precipitates with hydrogen chloride, bromide, or ferrocyanide, and is therefore probably cineol. The corresponding *chloride* crystallises from alcohol in felted needles, M.pt. 162° C., and unlike the iodide is readily soluble in alkali.

α-Iodomercuri-trans-terpineol,



This separates from benzene in glistening, colourless prisms, which are sensitive to light, become red at 120° C., and melt at 144° C. with decomposition. It is readily soluble in hot benzene, ether, alcohol, or concentrated potassium hydroxide solution, but less so in ethyl acetate. It may be obtained from the β-form by boiling the latter with organic solvents. The α-form combines with alcohol to form an *alcoholate*, $C_{10}H_{19}O_2IHg.C_2H_6O$, which crystallises from alcohol in glistening needles, turning red and melting at 123·5° C. It is reduced to trans-terpineol by sodium amalgam, or by electrolysis.

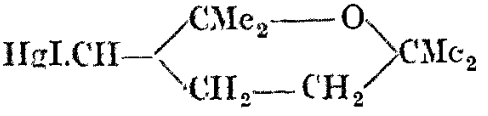
β-Iodomercuri-trans-terpineol, M.pt. 38° C., separates from organic solvents as an oil. It is very soluble in ether, ethyl acetate, alcohol, cold acetic acid, potassium hydroxide or iodide solution, with difficulty in cold benzene. It is reduced to trans-terpineol by sodium amalgam, and converted to the α-form by boiling with organic solvents. Since the α-form is readily converted into terpineol by mineral acids, it is probably the *cis* compound, whilst the β-form, which is only slowly decomposed, is the *trans* form.

α- and β-Mercuridimethylheptanediol iodides.—Dimethyl-

[1] Sand and Singer, *Ber.*, 1902, 35, 3170; *Annalen*, 1903, 329, 166.

heptenol, $CMe_2{=}CH.CH_2.CH_2.CMe_2OH$, readily dissolves in aqueous mercuric acetate solution, and addition of alkaline potassium iodide solution precipitates *two pairs* of *isomeric iodides*. One pair of iodides are soluble in alkali hydroxides, and have the constitution: $HO.CMe_2.CH(HgI).CH_2.CH_2.CMe_2.OH$. The *α-form* is a solid. M.pt. 124° to 125° C., and differs from the *β-form* in its solubility and stability towards acids.

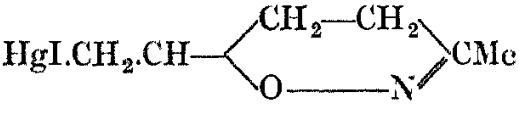
The second pair of iodides have the cyclic structure,



and are prepared as above, but with the addition of 10 per cent. potassium hydroxide before adding the potassium iodide. The *α-form* is a solid. M.pt. 108° to 110° C., whilst the *β-form* separates as an oil, and may be separated from the α-form by treating the mixture with cold alcohol. The oil is insoluble in concentrated potassium hydroxide solution, soluble in alcohol or ether, and slowly changes to the α-form in the presence of alkali.

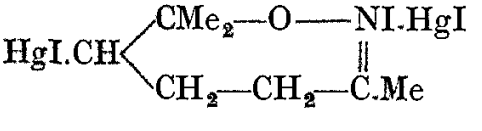
When the alkaline filtrate from these cyclic iodides is treated with carbon dioxide, the unstable *β-mercuridimethylheptanediol iodide* is precipitated as an oil. The latter when boiled or kept in the presence of alkali for some weeks changes to the stable α-modification, M.pt. 124° to 125° C.

Allylacetoxime,[1]—When allowed to react with mercuric acetate this compound yields an hydro-iso-oxazole derivative,



M.pt. 122° C., which may be crystallised from alcohol.

Methylheptenone oxime.—The products derived from this body depend on the conditions under which the reaction takes place. If the oxime be treated with mercuric acetate in presence of potassium bicarbonate and potassium iodide be added, a solid is obtained. This *product* when dissolved in methyl alcohol gives a precipitate with ether, which decomposes at 150° C. and probably has the constitution, $(C_8H_{14}ONIHg)_2HgI_2$. The alcohol-ether mother-liquors contain a more soluble *isomeride*, M.pt. 114° C. The above preparation when carried out in acid solution gives a mixture of compounds which are separated by treatment with cold alcohol. The *α-form* is a white, crystalline substance, M.pt. 94° C., yielding a *picrate*, sintering at 65° C., and melting at 78° to 80° C. The *β-form* is an insoluble, yellow, crystalline body, M.pt. 123° C., and probably has the constitution,

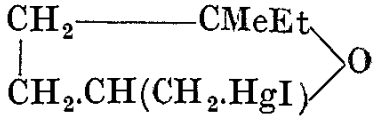


If potassium bromide be used for precipitation instead of the iodide, a *bromide*, $C_8H_{14}ONBr_3Hg_2$, M.pt. 123° C., is obtained; both the iodides

[1] Sand and Singer, *Annalen*, 1903, 329, 166.

and bromide have half their mercury precipitated as metal, when treated with hydrazine in the presence of alkali.

Ethylhexenol, $CH_2{=}CH.[CH_2]_2.C.MeEtOH$.[1]—This compound is dissolved in mercuric acetate solution and potassium iodide solution added, when an oil is precipitated; carbon dioxide is then passed in. Extraction with ether and evaporation of the solvent yields a crystalline compound, M.pt. 44° C., to which the following structure has been assigned :—

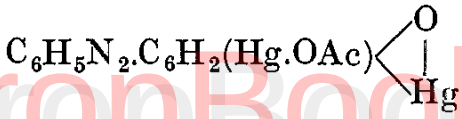


This appears to be a tetrahydrofurfurane derivative, since it gives an oily iodide with iodine, an aldehyde when oxidised by chromic acid, and is found to be saturated when treated with potassium permanganate. The iodide is reconverted to ethylhexenol when acted upon by hydrochloric acid.

DERIVATIVES OF AZO COMPOUNDS.

Mercuration of these compounds leads to dimercurated products if the ortho and para positions with respect to the amino or hydroxyl groups are available. No meta compounds are obtained.

Hydroxymercuri- acetoxymercuri- benzeneazo- phenol anhydride,[2]



DropBooks

Mercuric acetate (32 grams) in 150 c.c. of water and 20 c.c. of acetic acid is added to 10 grams of benzeneazo-phenol in 300 c.c. of alcohol. The red mixture is heated on the water-bath for six hours. An orange precipitate is formed, filtered, washed with dilute hot acetic acid, water, and alcohol, and dried at 110° C. Acetic acid is lost during this process, and to obtain a uniform product the substance must be dried at 120° C. It is purified by dissolving in 150 c.c. of glacial acetic acid and adding the solution to 400 c.c. of alcohol. The resulting product is washed with acetic acid—alcohol mixture and ether and dried at 120° C. It is the loss of acetic acid which accounts for the formation of an anhydride. A yellow-brown powder is finally isolated, which does not melt at 300° C. It is readily soluble in glacial acetic acid, insoluble in hot water, and sparingly soluble in alcohol, chloroform, ethyl acetate, benzene or nitrobenzene. When dissolved in 5 per cent. potassium hydroxide, and the hot filtered solution treated with saturated sodium chloride solution, the *dichloromercuri* compound is precipitated. The orange-red precipitate is washed with water and digested with hydrochloric acid, the colour changing to brick red. It is filtered, washed with hot water and alcohol, and dried at 110° C. It forms a dull red, amorphous powder, which does not melt at 300° C. and is insoluble in the usual solvents. The corresponding *dibromide* is a brownish-red powder, having similar properties to the dichloride.

[1] Sand and Singer, *loc. cit.*
[2] Smith and Mitchell, *Trans. Chem. Soc.*, 1908, 93, 847.

Diacetoxymercuri-2 : 4 : 6-tribromobenzeneazo-phenol, $C_6H_2Br_3.N_2.C_6H_2(Hg.OAc)_2.OH$.—Six grams of mercuric acetate (2 mols.) are dissolved in 20 c.c. of water containing 1 c.c. of acetic acid and a solution of 4 grams (1 mol.) of the hydroxyazo compound in 200 c.c. of alcohol added. After six hours' heating on the water-bath the precipitate is filtered, washed with dilute acid, then water, and dried. It is purified by recrystallisation from glacial acetic acid. It is a pale red, micro-crystalline powder, not melting below 300° C., and sparingly soluble in the usual solvents, with the exception of acetic acid. It loses acetic acid at 120° C.

Acetoxymercuri - benzeneazo - o - nitrophenol, $C_6H_5.N_2.C_6H_2(NO_2)(Hg.OAc).OH$, yields a pale yellow, crystalline powder, not melting below 300° C. and insoluble in all solvents except acetic acid. The *bromide* is a pale yellow powder.

Acetoxymercuri - benzeneazo - p - cresol,[1] $C_6H_5.N_2.C_7H_5(OH).Hg.OAc$.—Mercuric acetate in very dilute acetic acid is boiled under reflux with alcoholic benzeneazo-p-cresol for seven hours. It is purified by fractional precipitation from its acetic acid solution by water, and recrystallisation from glacial acetic acid. It crystallises in red-brown needles, M.pt. 269 to 270° C. with decomposition, and has similar solubilities to the above compounds. Its *chloride* melts with decomposition at 246 to 248° C. Dimroth prepared these compounds from acetoxymercuri-p-cresol and benzene diazonium chloride.[2]

8(?) - Acetoxymercuri - 2 - nitro - 4 - benzeneazo - α - naphthol.[3]—A mixture of 1 gram of the azo-α-naphthol in 250 c.c. of boiling water containing 5 c.c. of glacial acetic acid and 2·5 grams of mercuric acetate in 5 c.c. of warm water is heated for six hours on the water-bath. The mixture is filtered hot, washed with alcohol, boiling water, and hot dilute acetic acid. It is a lustrous, reddish-brown, crystalline mass, blackening at 220° C., but not fusing at 270° C., practically insoluble in all solvents.

8(?) - Acetoxymercuri - β - benzeneazo - α - naphthol, $C_6H_5.N_2.C_{10}H_5(OH).Hg.OAc$, is a brick-red powder, darkening at 180° C. and melting with decomposition at 208° C.

8(?) - Acetoxymercuri - 4 - nitro - 2 - benzeneazo - α - naphthol is a red substance having the appearance of amorphous phosphorus, melts with decomposition at 221° to 222° C., and is practically insoluble in all solvents.

Acetoxymercuri - bis - benzeneazo - α - naphthol, $(C_6H_5.N_2)_2.C_{10}H_4(OH).Hg.OAc$, forms lustrous black needles with a bronze lustre.

The following derivatives of azo dyes have been isolated :—[4]

Dihydroxymercuri-dihydroxyazobenzene sulphonic acid.—By the action of mercuric acetate on the mono-potassium salt of chrysoine in hot water or alcoholic solution containing a little acetic acid.

Dihydroxymercuri - β - naphthol-azobenzene sulphonic acid, by a similar method to the above, using "Orange II."

Mercuri-bis (hydroxymercuri - β - naphthol-azobenzene sulphonic acid), by heating "Orange II" in methyl alcohol containing

[1] Smith and Mitchell, *Trans. Chem. Soc.*, 1908, 93, 847; Dimroth, *Ber.*, 1902, 35, 2853.

[2] Dimroth's memoir also describes further reactions of benzene diazonium chloride with mercurated phenols and p-cresols.

[3] Mitchell and Smith, *Trans. Chem. Soc.*, 1909, 95, 1430.

[4] Proskouriakoff and Raiziss, *J. Amer. Chem. Soc.*, 1925, 47, 1974.

acetic acid with 2 equivalents of mercuric acetate. It is a red, amorphous powder.

Dihydroxymercuri-hydroxyazobenzene sulphonic acid, brownish-red powder.

Mercuri-bis (nitrobenzene-azosalicylic acid) is a light brown powder.

Compounds formed by diazotising p-acetoxymercurianiline, and coupling it with various compounds :—[1]

4-Acetoxymercuri-4′-dimethylaminoazobenzene yields brick-red crystals having a violet reflex, M.pt. 215° C. With sulphuric acid it forms reddish-brown solutions having a green fluorescence, and with nitric and hydrochloric acids sparingly soluble salts are formed.

4-Acetoxymercuri-4′-diethylaminoazobenzene consists of glittering orange-brown plates, becoming red at 120° C. and melting at 154·5° to 156° C. (corr.).

p-Acetoxymercuribenzeneazo-phenol, orange crystals, M.pt. 218° to 219° C. (corr.).

p-Acetoxymercuribenzeneazo-resorcinol.—Dark brown powder, sintering at 160° C. and melting with decomposition at 190° to 195° C.

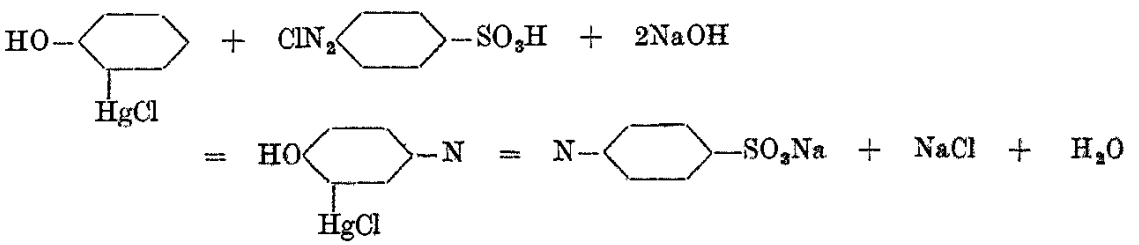
4-p-Acetoxymercuribenzeneazo-1-naphthylamine-5-sulphonic acid, brownish-black, micro-crystalline powder, decomposing at 280° C.

5-Acetoxymercuritoluene-2-azophenol is obtained from 5-acetoxymercuri-o-toluidine, M.pt. 204·5° to 205° C. (corr.).

DropBooks

DERIVATIVES OF HYDROXYAZOBENZENES.[2]

Sodium-3-chloromercuri-4-hydroxy-azobenzene-4′-sulphonate is formed by diazotising sulphanilic acid and adding the diazotised solution to a cold solution of o-chloromercuriphenol in sodium hydroxide. The coupling requires about four hours for completion. The mixture is then acidified with acetic acid, when the sodium salt of the azo compound separates as a heavy, orange-yellow precipitate. The product is recrystallised from hot water, air-dried, and then dried in a vacuum dryer at 50° C. Since the C—Hg linkage is easily split it is impossible to obtain the free acid. The reaction is represented as follows :—



In a similar manner o-chloromercuriphenol has been coupled with the following diazotised aromatic acids :—

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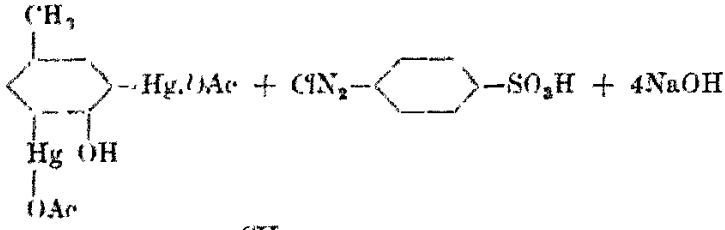
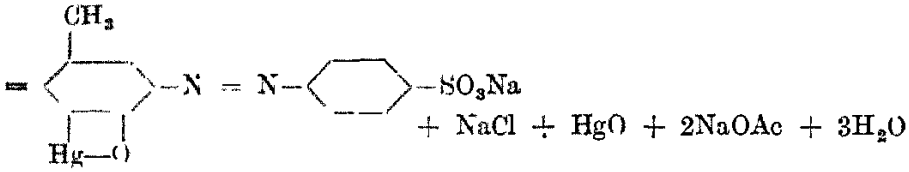
[1] Jacobs and Heidelberger, *J. Biol. Chem.*, 1915, **20**, 513.
[2] Whitmore, Hanson, and Leuck, *J. Amer. Chem. Soc.*, 1926, **48**, 1013.

Amino Acid.	Product.	Colour.
Metanilic	Sodium salt	Yellow.
Naphthionic	Sodium salt	Orange.
Anthranilic	Free acid	Red.
m-Aminobenzoic	Free acid	Red.
p-Aminobenzoic	Free acid	Red-yellow.

Sodium anhydro - 2 - hydroxy - 3 - hydroxymercuri - 5 - methyl - azobenzene - 4′ - sulphonate.—In this case 2 : 6-diacetoxymercuri-p-cresol, in sodium hydroxide solution, is added to the diazotised sulphanilic acid. The mixture is stirred for ten hours and cooled in ice during this period. Acidification with acetic acid precipitates the slightly soluble, yellow sodium salt. It is purified by crystallisation from water. Strong acids remove the mercury completely, so that the free acid cannot be obtained, and attempts to prepare the chloride have been unsuccessful. The reaction is represented as follows :—





Anhydro - 2 - hydroxy - 3 - hydroxymercuri - 5 - methyl-azobenzene - 2′ - carboxylic acid is prepared using anthranilic instead of sulphanilic acid. The free acid is deep red, but no method is available for its purification, owing to its insolubility in all except basic solvents. The purest product is obtained when exact quantities of carefully purified anthranilic acid and mercurated cresol are used.

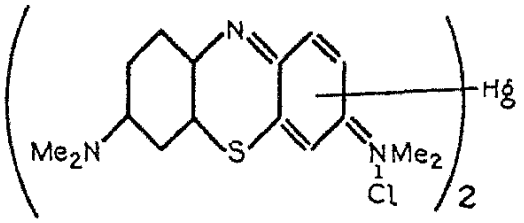
In a similar manner, **anhydro-2-hydroxy-3-hydroxymercuri-5-methyl-azobenzene-4′-carboxylic acid** is prepared, and its properties are very like those of its isomer.

DERIVATIVES OF METHYLENE BLUE.[1]

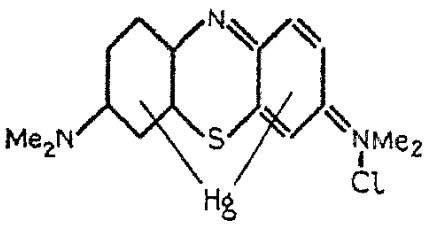
The work done on this compound, which presents numerous difficulties, is admitted by Chalkley to be very incomplete. To obtain complete mercuration, a large excess of mercuric acetate has to be used. With three molecular equivalents of the latter, benzoyl-leucomethylene blue yields an *acetoxymercuri compound* in the form of a white powder, which gives a yellow *sulphide* with hydrogen sulphide. Methylene blue acetate heated with 15 mols. of mercuric acetate in aqueous solution in the presence of acetic acid gives two organic mercury

[1] Chalkley, *J. Amer. Chem. Soc.*, 1925, 47, 2055; see Kharasch and Piccard, *ibid.*; *Chem. Soc.*, 1920, 42, 1855.

compounds, I., II., the former readily going into colloidal suspension, and consequently is difficult to handle.[1]



(I)



(II)

DERIVATIVES OF PHTHALEINS.[2]

Hydroxymercuri phenolphthalein.—To a solution of 3 grams of phenolphthalein in 25 c.c. Normal sodium hydroxide, about 125 c.c. of water are added and the solution boiled with 3 grams of yellow mercuric oxide for three hours. The mixture is then allowed to settle, the liquor poured off and centrifuged to remove traces of sediment. Carbon dioxide is passed in, and the mercurated product separates as a purplish, milky precipitate, which is separated by centrifuging. It is washed with alcohol and dried at 110° C. It is insoluble in all the usual solvents, except glacial acetic acid, in which it gives turbid solutions. It cannot be crystallised, and gives the same colour with alkali as phenolphthalein.

Triacetoxymercuri phenolphthalein.—Three grams of phenolphthalein in 50 c.c. of alcohol are mixed with a filtered solution from 25 grams of mercuric acetate in 50 c.c. of water and 50 c.c. of glacial acetic acid. After standing overnight, any mercurous acetate is removed, and the liquid heated on the water-bath for three hours. After twenty-four hours the residue is removed and washed with alcohol, then with water containing a little acetic acid, and finally with water. The crystals are dried in the air for several days, then heated for one hour at 100° C. It forms bladed crystals, insoluble in the usual solvents, dissolving in sodium hydroxide with the production of a deep-blue colour.

Trihydroxymercuri phenolsulphone-phthalein is prepared in a similar manner to hydroxymercuri phenolphthalein. It is a purplish powder having a bronze lustre. When mercuric acetate reacts with phenolsulphone phthalein in acetic acid solution, a mixture of hydroxymercuri and acetoxymercuri derivatives is produced.

Diacetoxymercuri-o-cresolphthalein is prepared in the usual manner, more mercurous acetate being formed than with the previous derivatives. It is a yellow, granular substance, which cannot be recrystallised.

Hydroxymercuri and dihydroxymercuri fluorescein.—Fluorescein, 3·5 grams, in 200 c.c. of one-tenth Normal sodium hydroxide is treated with 5 grams of mercuric oxide, and the mixture boiled for four hours, water being added to replace that lost by evaporation. It is then clarified by centrifuging, and evaporated to dryness, an iridescent, green, scaly product being obtained. This is the monomercurated product. The *dihydroxymercuri* compound is formed when 10 grams

[1] Compounds of the *acridine* series are dealt with in American Patent, 1259517, and those of the *safranine* series in German Patent, 286097.

[2] White, *J. Amer. Chem. Soc.*, 1920, 42, 2355; German Patent, 308335.

of mercuric oxide are used in the above preparation. Treatment with hydrochloric acid yields *chloromercuri* derivatives.

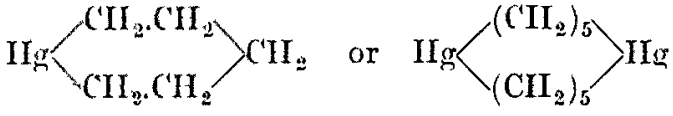
The mercuration of fluorescein by mercuric acetate in acetic acid solution leads to the production of a mixture of *tetrahydroxymercuri* and *tetra-acetoxymercuri fluorescein*, the latter predominating. No attempt seems to have been made to separate these products.

Hydroxymercuri-dibromofluorescein.—Dibromofluorescein (49 grams) and 8 grams of sodium hydroxide are dissolved in 50 c.c. of water and the solution made up to 200 c.c. This is stirred and treated with 12·5 c.c. of glacial acetic acid until an even pasty precipitate is formed. A solution prepared from 22·5 grams of mercuric oxide in 25 c.c. of glacial acetic acid and 50 c.c. of water is diluted to 100 c.c., and added to the former solution, the whole being diluted to 500 c.c. The mixture is boiled 4·5 to 6 hours, a quantitative yield being obtained. The precipitate is collected and washed by centrifuging, a red powder being isolated, which is insoluble in the usual solvents, but gives a deep cherry-red solution in sodium hydroxide.[1]

Hydroxymercuri-salicylsulphone-phthalein.[2]—Salicylsulphone-phthalein (salicyl red) is dissolved in sufficient Normal sodium hydroxide to form the di-sodium salt, then treated with a solution of mercuric acetate containing a few drops of acetic acid, and the mixture boiled until a test gives no reaction with ammonium sulphide. It is then filtered and poured into dilute hydrochloric acid. The mercurated product separates as a brown powder.

CYCLOMERCURIPOLYMETHYLENES.[3]

Cyclomercuri pentamethylene,



A mixture of 30 grams of 1 : 5-dibromopentane, 100 grams of benzene, 3 grams of ethyl acetate, and 900 grams of 1 per cent. sodium amalgam is shaken for twenty-four hours in a pressure flask at 75° C. The solvent layer is washed, evaporated, and the residue extracted with absolute alcohol, from which 23 grams of waxy product are obtained. This is extracted with light petroleum and ether, 6·5 grams of solid, M.pt. 41° C., remaining behind. Evaporation of the extract gives 2·5 grams of crystals, M.pt. 120° C., which are separated from an oil.

Cyclomercuri pentamethylene, M.pt. 120° C., forms hard, white, rhombic, doubly refracting crystals from a mixture of benzene-light petroleum. It is readily soluble in cold ether, light petroleum, or benzene, with difficulty in water. Its molecular weight as determined by the ebullioscopic method is about 360 (270 calc.), and this appears to correspond to a simple ring. v. Braun, however, points out that a comparison of the boiling-points of the pentamethylene series of com-

[1] German Patent, 201903, deals with a process for preparing mercurated salts of fluorescein, see Dimroth, *Ber.*, 1902, 35, 2853. The products obtained may be used directly for dyeing. The dyestuffs dye cotton in the following manner: Chromium mordant—brown red; iron mordant—reddish brown; uranium mordant—red; nickel and cobalt mordant—red; alkaline earth mordant—red; cerium mordant—light red.

[2] Harden, *J. Amer. Chem. Soc.*, 1927, 49, 3141.

[3] v. Braun, *Ber.*, 1913, 46, 1792; 1914, 47, 490; Hilpert and Grüttner, *Ber.*, 1914, 47, 186, 177.

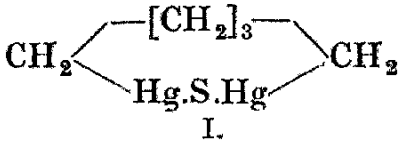
pounds, $(CH_2)_5>R$, with those of the series Et—R—Et, where R may be O, CH_2, NH_2S, or Hg, indicates that cyclomercuri-pentamethylene should have a boiling-point of about 210° C.; that it should distil without decomposition under diminished pressure, and probably without decomposition under ordinary pressure. He therefore considers the product, M.pt. 120° C., to be a polymeride of the true compound. The following is the list of compounds upon which the argument is based:—

Et—O—Et,	B.pt. 35° C.	$(CH_2)_5>O$,	B.pt. 88° C.
Et—CH_2—Et,	B.pt. 36° C.	$(CH_2)_5>CH_2$,	B.pt. 80° C.
Et—NH—Et,	B.pt. 55° C.	$(CH_2)_5>NH$,	B.pt. 105° C.
Et—S—Et,	B.pt. 92° C.	$(CH_2)_5>S$,	B.pt. 141° C.
Et—Hg—Et,	B.pt. 159° C.	$(CH_2)_5>Hg$,	B.pt. 210° C. (about).

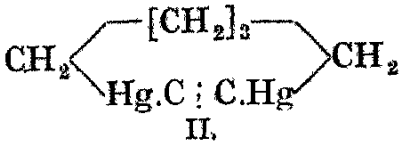
The *compound*, M.pt. 41° C., probably a polymer, may be recrystallised from much ether, and obtained as a white powder. Its molecular weight is four times that of the compound. M.pt. 120° C., and the oil obtained has six times the molecular weight of the latter.

All these compounds give the same products when treated with bromine, iodine, or mercuric halides. With iodine in benzene solution theoretical yields of pentamethylene-dimercuri-iodide and di-iodopentane are obtained.

Pentamethylene-1 : 5-dimercuri-dibromide, $C_5H_{10}Hg_2Br_2$.—The Grignard solution from 20 grams of 1 : 5-dibromopentane, 4·1 grams of magnesium, and a trace of iodine, after standing for twelve hours is warmed on the water-bath, and treated with 66 grams of mercuric bromide in ether, in 5-gram portions. The mixture is then boiled for an hour and decomposed by 1 per cent. hydrochloric acid. The ether is removed at 60° C., and the product again treated with 1 per cent. hydrochloric acid at 60° C. It is filtered hot, washed with cold water, then with alcohol. The residue is added in small portions to 500 grams of boiling water, digested for fifteen minutes, filtered boiling hot, washed with cold water, alcohol, and ether, and dried at 100° C. Yield of crude product, 49 grams or 8·94 per cent. It crystallises from toluene in doubly refracting needles, M.pt. 150° C., very soluble in pyridine, aniline, or dimethylaniline in the cold, and may be precipitated by the addition of light petroleum. It is less soluble in hot alcohol, acetone, boiling toluene or xylene, and with difficulty in hot water, hot carbon tetrachloride, ether, or petroleum ether. When boiled for one hour with alcoholic potassium iodide it yields the *di-iodide*, sintering at 115° C. and melting at 117° C. It crystallises best from alcohol-benzene, and is less soluble than the dibromide. Prolonged boiling in benzene solution gives mercuric iodide and di-iodopentane. Hydrogen sulphide precipitates a quantitative yield of the *sulphide* from a pyridine solution of the dibromide. It is a snow-white, insoluble, odourless powder, having the constitution (I.). By passing acetylene into a solution of the pure dinitrate in alcoholic ammonia, for one hour at 0° C., an *acetylide* (II.) is formed. It is a white powder, which takes fire on heating, is insoluble in the usual organic solvents, and heated in benzene yields mercuric iodide and di-iodopentane.



I.



II.

The *dihydroxide* crystallises in hair-fine, white needles, and is isolated by boiling the bromide with silver oxide in 80 per cent. alcohol for twenty hours. Treatment of the hydroxide in 50 per cent. alcohol with sulphuric acid precipitates the *sulphate* as microscopic white needles, suddenly blackening above 150° C. The dibromide with silver nitrate gives the *dinitrate*, from which the *dichloride* is prepared. It crystallises in white needles, M.pt. 184° C. The following compounds are also mentioned: *oxalate*, *succinate*, *ferrocyanide*, white precipitates, and the *azelate*, white scales.

Pentamethylene - 1 : 5 - dimercuridiphenyl, $C_6H_5Hg.(CH_2)_5.Hg.C_6H_5$.—This remarkable compound is prepared by treating magnesium phenyl bromide (4 times the calculated amount) with dry, powdered pentamethylene-1 : 5-dimercuric dibromide in small portions. The reaction is completed by boiling for one hour on the water-bath. The mixture is decomposed by dilute sulphuric acid, and worked up in the usual manner.

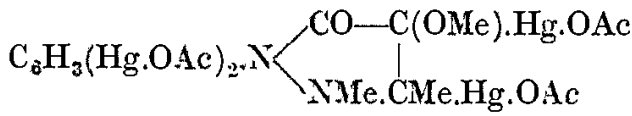
It is a colourless, viscous oil, decomposing when heated *in vacuo* at 180° C. It quickly decolorises a solution of iodine in benzene, with formation of the above di-iodide, and prolonged boiling with an excess of the iodine solution gives mercuric iodide, 1 : 5-di-iodopentane and iodobenzene.

It will be seen from the above reactions that the mercury atoms in these compounds are very firmly attached, whilst the halogen atoms are very reactive.

DERIVATIVES OF THE PYRAZOLONE GROUP.[1]

When the phenyl-5-pyrazolones are treated with mercuric acetate in alcoholic solution, four acetoxymercuri groups are introduced into the molecule, together with a methoxy group. If, however, the hydrogen in the 4-position be substituted by halogen or methyl groups, mercuration only takes place at 160° C.

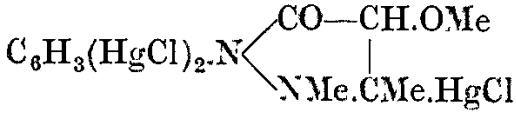
3 : 4 - Diacetoxymercuri - 4 - methoxy - 1 - diacetoxymercuriphenyl - 2 : 3 - dimethyl - 5 - pyrazolone,



One gram of phenyldimethylpyrazolone (1 mol.) is dissolved in 5 c.c. of methyl alcohol and 7·28 grams of mercuric acetate (4 mols.) in 45 c.c. of methyl alcohol poured in. The temperature is maintained at 60° C. and rhombic plates begin to separate in fifteen minutes, and after about two hours the product is filtered off. It is washed several times with warm methyl alcohol, faintly acidified with acetic acid, then dried *in vacuo* over sulphuric acid. Yield 6·5 grams, 97·4 per cent. The substance sinters between 200° and 205° C., then decomposes with gas evolution. It is insoluble in most organic solvents, somewhat soluble in hot methyl or ethyl alcohol, especially if these contain a trace of acetic acid, and easily soluble in water faintly acidified with acetic acid. It is also soluble in ammonium hydroxide and amine bases such as ethylenediamine. Ammonium sulphide removes the mercury in the 4-position.

[1] Schrauth and Bauerschmidt, *Ber.*, 1914, 47, 2736; see also, Paderi, *Chem. Zentr.* 1919, iii. 226; Oliveri-Mandalà, *Gazzetta*, 1921, 51, i. 125.

This is probably due to the adjacent carbonyl group, since it is also removed by dilute hydrochloric acid when **3-chloromercuri-4-methoxy-1-dichloromercuriphenyl-2:3-dimethyl-5-pyrazolone** is produced.



The latter is prepared by suspending 2 grams of powdered tetra-acetoxymercuri compound in about 40 c.c. of a quarter Normal hydrochloric acid, and shaking on a machine for twelve hours. It is filtered and washed free from chloride and dried *in vacuo* over phosphorus pentoxide at 100° C. The substance is a micro-crystalline powder, slightly soluble in acetone, but insoluble in all other solvents. It does not melt, and is not immediately blackened by ammonium sulphide.

3:4-Diacetoxymercuri-4-ethoxy-1-diacetoxymercuriphenyl-2:3-dimethyl-5-pyrazolone is prepared in a similar manner to the 4-methoxy compound, but the methyl alcohol in the latter preparation is now replaced by ethyl alcohol. Yield 96·6 per cent. It forms small, colourless needles which crystallise with 1 mol. of water, which may be removed by heating *in vacuo* over phosphorus pentoxide at 110° C. It has similar solubilities to the methoxy compound, and hydrochloric acid removes the mercury in the 4-position.

3:4-Diacetoxymercuri-4-methoxy-1-diacetoxymercuriphenyl-3-methyl-2-ethyl-5-pyrazolone,

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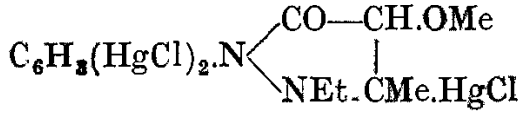
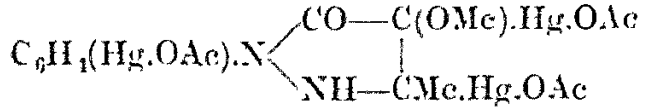
One gram of phenylethylmethylpyrazolone in a little methyl alcohol is treated with a solution of 7 grams of 90 per cent. mercuric acetate (4 mols.) in 50 c.c. of methyl alcohol. The mixture is maintained at 60° C. and crystals separate in twenty-five minutes, are filtered after two hours, washed with acidified methyl alcohol, and dried. Yield 6·1 grams, 90 per cent. The substance has similar solubilities to the above 4-methoxy compound and decomposes above 200° C. It crystallises in prismatic needles, from which the mercury in the 4-position is removed by hydrochloric acid in the usual way, **3-Chloromercuri-4-methoxy-1-dichloromercuriphenyl-3-methyl-2-ethyl-5-pyrazolone** being obtained, which has the structure:



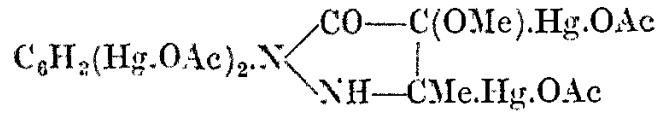
In a similar manner 1-p-tolyl-2:3-dimethyl-5-pyrazolone and 1-o-tolyl-3-methyl-2-ethyl-5-pyrazolone in methyl alcohol solution are converted into **3:4-diacetoxymercuri-4-methoxy-1-[diacetoxymercuri-p-tolyl] 2:3-dimethyl-5-pyrazolone** and the corresponding **3:4-diacetoxymercuri-4-methoxy-1-[diacetoxymercuri-o-tolyl]-3-methyl-2-ethylpyrazolone**, both of which lose mercury from the 4-position by the action of hydrochloric acid, yielding ***trichloromercuri*** derivatives.

3 : 4 - Diacetoxymercuri - 4 - methoxy - 1 - acetoxymercuriphenyl - 3 - methyl - 5 - pyrazolone,



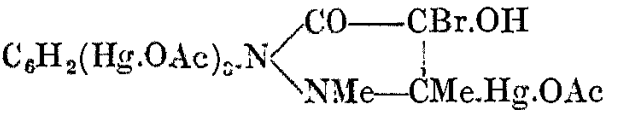
A 66 per cent. yield is obtained by carrying out the mercuration in the usual manner, but no heating is necessary, the reaction being complete in several hours at room temperature. From the mother-liquor a further quantity may be obtained, raising the yield to 90 per cent. The *crystals melt at 167° C. with decomposition, and contain 1 mol. of* water of crystallisation, which may be removed by heating *in vacuo* over phosphorus pentoxide at 138° C. The mercury in the 4-position is removed by ammonium sulphide or hydrochloric acid, a *dichloromercuri* compound being obtained which is somewhat soluble in acetone.

If, however, 1-phenyl-3-methyl-5-pyrazolone be mercurated in boiling methyl alcohol solution for three hours, **3-diacetoxymercuri-4-methoxy-1-diacetoxymercuriphenyl-3-methyl-5-pyrazolone** is formed :



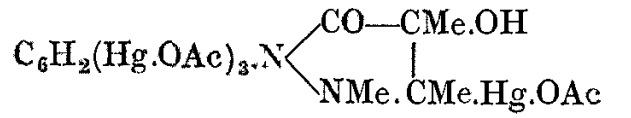
It is a crystalline product, decomposing at 225° C., sparingly soluble or insoluble in the usual solvents.

4-Bromo-4-hydroxy-3-acetoxymercuri-1-triacetoxymercuriphenyl-2 : 3-dimethyl-5-pyrazolone,



Two grams of 4-bromo-1-phenyl-2 : 3-dimethyl-5-pyrazolone (1 mol.) and 10·5 grams of mercuric acetate (4 mols., 90 per cent.) are heated for thirty minutes in an oil-bath at 160° C. The melt is cooled, extracted with alcohol, the solution boiled with charcoal, filtered, and treated with ether. The white precipitate is filtered, washed with ether, and dried. It is a hygroscopic substance, readily soluble in cold water, less soluble in methyl or ethyl alcohol faintly acidified with acetic acid. It decomposes with gas evolution at 225° C., and is unaffected by ammonium sulphide unless boiled. From its aqueous solution sodium chloride precipitates an insoluble *chloride*, and sodium hydroxide the corresponding *hydroxide*.

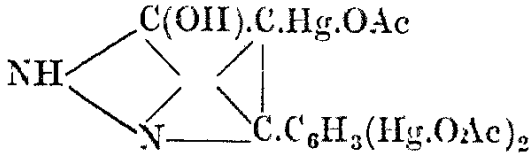
4 - Hydroxy - 3 - acetoxymercuri - 1 - triacetoxymercuriphenyl - 2 : 3 : 4 - trimethyl - 5 - pyrazolone,



This is formed from 1-phenyl-2 : 3 : 4-trimethyl-5-pyrazolone in the same manner as the preceding compound. It melts at 237° C. (corr.) with strong decomposition, and has similar properties to the bromo derivative. When treated with hydrochloric acid it yields **4-hydroxy-**

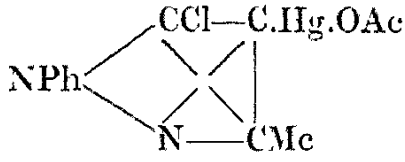
3-chloromercuri-1-trichloromercuriphenyl-2 : 3 : 4-trimethyl-5-pyrazolone, which decomposes at about 245° C.

4-Acetoxymercuri-3-diacetoxymercuriphenyl-5-pyrazolone,



The reaction between 3-methyl-5-pyrazolone (1 mol.) and mercuric acetate (3 mols.) takes place when the two are boiled for three hours in methyl alcohol solution. The effect of the possibility of enolisation is marked by the absence of any methoxy group in the product. In methyl or ethyl alcohol strongly acidified with acetic acid it is only soluble with difficulty, and from these solvents it crystallises in colourless needles, which decompose about 250° C. Treated with hydrochloric acid, it is converted into a *dichloromercuri* compound, decomposing near 240° C. With ammonium sulphide, these two compounds do not blacken immediately.

5-Chloro-4-acetoxymercuri-1-phenyl-3-methylpyrazolone,



This compound is prepared as the preceding one, from 5-chloro-1-phenyl-3-methylpyrazole. It melts at 123° C., is readily soluble in water, alcohol, and all the usual solvents. It is unaffected by cold ammonium sulphide, but with hydrochloric acid yields a *dichloromercuri* compound, needles, M.pt. 165° C.

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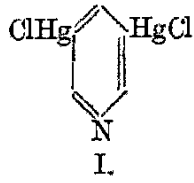
DERIVATIVES OF PYRIDINE.[1]

Pyridine and mercuric acetate when heated at 175° to 180° C. for 2·5 hours, and the reaction mixture diluted with 5 to 6 volumes of water, followed by the addition of sodium chloride give **3 : 5-dichloromercuri pyridine** (I.) as a pale brown, amorphous, odourless powder, decomposing at 220° C. Bromine in sodium bromide solution converts it into 3 : 5-dibromopyridine. The mother-liquors from the dichloromercuri compound yield **3-iodomercuri pyridine** (II.) when treated with sodium iodide. The product is a yellow, amorphous powder, M.pt. 68° to 69° C., which forms 3-bromopyridine with bromine in sodium bromide.



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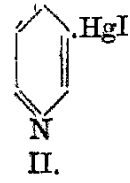


II.

DERIVATIVES OF FURANE AND PYRROLE.

Tetra-acetoxymercuri-furane[2] is formed when mercuric acetate reacts with furane. It decomposes at 226° to 228° C. and is converted by potassium hydroxide into the *tetrahydroxy-compound*, decomposing

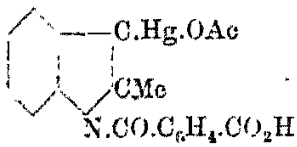
[1] Sachs and Eberhartinger, *Ber.*, 1923, 56, [B], 2223.
[2] Ciusa and Grillo, *Gazzetta*, 1927, 57, 322.

at 210° C. The latter with sodium chloride gives *tetrachloromercuri-furane*, decomposing at 235° C., iodine transforming this into tetra-iodo-furane. A *monoacetoxymercuri-furane* has been reported, but its existence seems doubtful.

Pyrrole likewise forms *tetrachloro* and *tetra-acetoxy* derivatives, the former yielding tetra-iodopyrrole when treated with iodine in potassium iodide.

DERIVATIVES OF THE INDOLE SERIES.[1]

3-Acetoxymercuri-2-methyl-1-phthalyl-indole,

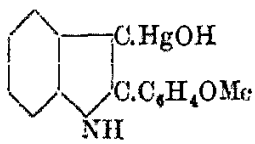


Methylphthalylindole (1·4 parts) is dissolved in 30 parts of hot alcohol, and mixed with a solution of 1·9 parts of mercuric acetate in 10 parts of alcohol. The product separates immediately as a pale reddish precipitate. After cooling, it is filtered and washed with alcohol and ether. It is insoluble in the usual solvents, and when heated with mineral acids methylphthalylindole is formed.

3-Acetoxymercuri-1-methylindole.—To a solution of 3·8 parts of mercuric acetate in 20 parts of methyl alcohol, a methyl alcohol solution of 1·3 parts of *N-methylindole is added.* The compound separates as a white, crystalline mass, which is washed with methyl alcohol and ether. It is readily soluble in hot alcohol, benzene, or acetone, crystallising in fine needles as the solutions cool. It is decomposed by heating with dilute mineral acids.

3-Hydroxymercuri-2-carboxy-1-methylindole is prepared from N-methylindole carboxylic acid in the usual manner. It is insoluble in the usual organic solvents, but dissolves readily in alkalies. Hot dilute mineral acids split off the mercury.

3-Hydroxymercuri-2-anisylindole,



Anisylindole (1·1 parts) in 100 parts of hot alcohol is mixed with 1·8 parts of mercuric acetate in 10 parts of alcohol. A turbidity appears, and the mixture is warmed for a short time on the water-bath, when the product separates as a brown precipitate. It has similar properties to the preceding compounds.

A product has also been isolated from 2-*methyl indole* (methylketole) as a pale yellow precipitate, resembling the other indole derivatives. Treatment of its aqueous suspension with hydrogen sulphide immediately gives black mercuric sulphide.

DERIVATIVES OF QUINOLINE.[2]

Hydroxymercuri-2-hydroxyquinoline-8-carboxylic acid.—The acid (20·6 parts) is suspended in about 1000 parts of water, and the mercuric oxide from 13·5 parts of mercuric chloride stirred in. The

[1] German Patent, 236893. [2] German Patent, 289246.

mass is boiled until a portion no longer gives a precipitate of mercuric oxide when treated with sodium hydroxide. The compound is isolated as a dark yellow, water-insoluble precipitate. The acid is insoluble in alcohol, ether, and benzene, and after warming with hydrochloric acid, ammonium sulphide precipitates mercuric sulphide.

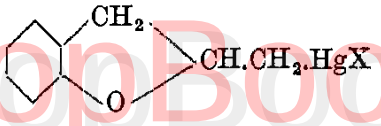
Hydroxymercuri-8-hydroxyquinoline-5-sulphonic acid is prepared in a similar manner. The free acid is bright yellow, sparingly soluble in water and insoluble in alcohol, ether, or benzene.

Hydroxymercuri-2-phenylquinoline-4-carboxylic acid.—Ten grams of the acid are mixed with 13·3 grams of mercuric acetate in aqueous solution, and the whole heated until a clear solution is obtained with sodium hydroxide. The product is then filtered, washed with water and dissolved in very dilute sodium hydroxide, excess being avoided, and the solution treated with alcohol. The *sodium salt* is precipitated, and has a similar solubility to the preceding compound. The preparation may also be carried out using mercuric oxide in place of acetate.

Using the above methods, compounds have also been obtained from quinoline-8-sulphonic acid and 8-hydroxyquinoline.

DERIVATIVES OF DIHYDROBENZOFURANES.[1]

The addition of mercuric salts to o-allylphenols leads to the production of a series of mercurated dihydrobenzofuranes of the general formula:



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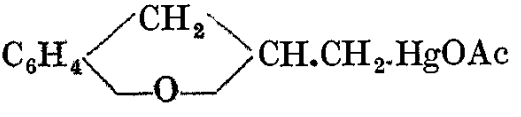
In comparison with other mercury salt-olefine compounds, these bodies are very stable towards acids. They yield compounds of the type R_2Hg when reduced by sodium amalgam, and the corresponding iodide when treated with potassium iodide. No reasonable molecular formula has been devised for these compounds, which completely fits in with the facts, so that they are at present merely written as additive formulæ.

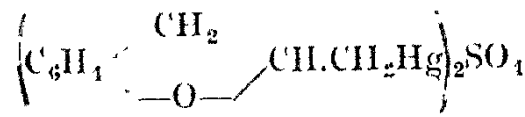
1-Acetoxymercurimethyl-1 : 2-dihydrobenzofurane,



This is prepared by suspending o-allylphenol in water, and adding an aqueous solution of mercuric acetate. It crystallises in colourless plates, M.pt. 80° to 81° C. The corresponding *chloride* may be obtained by adding sodium chloride to the above compound or by replacing the mercuric acetate by mercuric chloride. It melts at 137° C. The *bromide* crystallises in lustrous crystals, M.pt. 122° C., and the *iodide* in colourless plates, M.pt. 114° to 115·5° C.

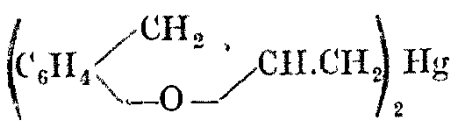
[1] Since it has not been definitely decided whether these compounds are "molecular" substances or merely addition compounds, only general directions have been given for their preparation. Evidence at present points to the latter type. Adams, Roman, and Sperry, *J. Amer. Chem. Soc.*, 1922, 44, 1781; Mills and Adams, *ibid.*, 1923, 45, 1842.

1 : 1-Sulphato-mercuridimethylene-bis-1 : 2-dihydrobenzofurane,



o-Allylphenol is carefully added to a solution of mercuric oxide in dilute sulphuric acid. The product melts at 123° C. with decomposition.

1 : 1-Mercuridimethylene-bis-1 : 2-dihydrobenzofurane,



This is obtained in colourless crystals, M.pt. 93° C., when 1-chloromethyl-1 : 2-dihydrobenzofurane is reduced by sodium amalgam in ethyl alcohol solution.

The following is given as a general method of preparation of substituted 1-mercurimethyl-1 : 2-dihydrobenzofuranes. Ten grams of a substituted o-allylphenol are slowly added to an aqueous solution containing one molecular equivalent of mercuric acetate or chloride. With the latter, a saturated solution is used, and the phenol slowly added until a flocculent precipitate is obtained, the operation lasting one hour. The stirring is maintained until the oil solidifies. With mercuric acetate, about 10 grams of salt are used with each 100 c.c. of water.

The following mercurated 1 : 2-dihydrobenzofuranes have been prepared by the addition of mercuric salts to o-allylphenols: 1-*Acetoxymercurimethyl-6-methyl-*, M.pt. 113° C.; 1-*chloromercurimethyl-6-methyl-*, M.pt. 91° C.; 1-*acetoxymercurimethyl-5-methyl-*, oil; 1-*chloromercurimethyl-5-methyl-*, M.pt. 127·5° C.; 1-*acetoxymercurimethyl-4-methyl-*, oil; 1-*chloromercurimethyl-4-methyl-*, M.pt. 99·5° C.; 1-*acetoxymercurimethyl-4-bromo-*, oil; 1-*chloromercurimethyl-4-bromo-*, M.pt. 108° C.; 1-*chloromercurimethyl-6-carboxy-*, M.pt. 200° C. with decomposition; 1-*chloromercurimethyl-6-carbomethoxy-*, M.pt. 107° C. with decomposition; 1-*chloromercurimethyl-4-carboxy-*, M.pt. 212° to 213° C. with decomposition; 1-*chloromercurimethyl-4-carboxyvinylene-*, M.pt. 300° C. with decomposition.

The following is a general method for conversion of 1-chloromercuri- or 1-acetoxymercurimethyl-1 : 2-dihydro-benzofuranes into the corresponding bromides and iodides: A solution of 5 grams of the chloro or acetoxymercuri compound in absolute alcohol is mixed with a boiling solution of alcohol containing one molecular equivalent of the potassium halide. The compound separates on cooling, is washed and crystallised from alcohol. The following mercurated 1 : 2-dihydrobenzofuranes are thus obtained: 1-*Iodomercurimethyl-6-methyl-*, M.pt. 88° C.; 1-*iodomercurimethyl-5-methyl-*, M.pt. 131·5° C.; 1-*iodomercurimethyl-4-methyl-*, M.pt. 94° C.; 1-*bromomercurimethyl-4-bromo-*, M.pt. 93° C.; 1-*iodomercurimethyl-4-bromo-*, M.pt. 101° C.

1-Hydroxymercurimethyl-1 : 2-dihydrobenzofuranes are obtained by treating 10 grams of the corresponding chloro compounds with one molecular equivalent of sodium hydroxide in 50 c.c. of warm absolute alcohol. The products are recrystallised from 95 per cent. alcohol. The following are recorded: 1-*Hydroxymercurimethyl-*, M.pt. 152° C.; 1-*hydroxy-*

mercurimethyl-6-methyl-, thick oil; 1-*hydroxymercurimethyl-4-methyl-*, M.pt. 149° C.

When the above compounds are dissolved in hot alcohol, diluted with hot water, and a hot aqueous alcoholic solution of the requisite acid added, the following compounds are obtained: 1-*Tartrato-di-mercurimethyl-*, M.pt. 192° C. with decomposition; 1-*oxalato-di-mercurimethyl-*, M.pt. 175° C.; 1-*p-nitrobenzatomercurimethyl-*, M.pt. 148° C.; 1-*p-nitrobenzatomercurimethyl-6-methyl-*, M.pt. 162·5° C.; 1-*p-nitrobenzatomercurimethyl-4-methyl-*, M.pt. 136·5° C.

1-Chloromercurimethyl-1:2-dihydrobenzofuranes, when added to saturated solutions of potassium cyanide or thiocyanate in absolute alcohol, yields: 1-*Thiocyanatomercurimethyl-*, M.pt. 112·5° C.; 1-*cyanomercurimethyl-*, M.pt. 162° C.; 1-*thiocyanatomercurimethyl-4-methyl-*, M.pt. 102·5° C.; 1-*cyanomercurimethyl-4-methyl-*, M.pt. 148° C.

The following compounds have also been described: 1-*Sodiumthiosulphatomercurimethyl-1:2-dihydrobenzofuranes*, 1-*sodiumthiosulphatomercurimethyl-4-methyl-*, and 1:1-*mercuridimethylene-bis-1-methyl-1:2-dihydrobenzofuranes*.

DERIVATIVES CONTAINING MERCURY AND SELENIUM.

Products from 2:4-Diphenyl-selenophene.[1]

5-Chloromercuri-2:4-diphenyl-selenophene.—An alcoholic solution of the selenophene is treated with the mercuric halide in the presence of sodium acetate, and the solution mechanically stirred for twelve hours. After a further twelve hours' standing, a 90 per cent. yield of product is obtained, which melts at 224° C. (corr.) after crystallisation. When heated under reflux for an hour with aqueous bromine it is converted to tribromo-diphenyl-selenophene. An acetone solution of potassium bromide gives the 5-bromomercuri derivative and mercuri-bis-(2:4-diphenyl-selenophene-5).

5-Bromomercuri-2:4-diphenyl-selenophene is prepared by the methods outlined above or by heating the mercuri-bis compound for ten minutes with mercuric bromide in acetone solution. It crystallises from alcohol in microscopic, colourless, felted hairs, M.pt. 215° C. (corr.), soluble in benzene, toluene, or glacial acetic acid. When its toluene solution is boiled, it decomposes with formation of diphenyl-selenophene and mercurous bromide.

5-Iodomercuri-2:4-diphenyl-selenophene cannot be formed by the action of mercuric iodide and sodium acetate on 2:4-diphenyl-selenophene, or by sodium iodide upon the 5-chloromercuri compound. A 30 per cent. yield is obtained when the mercuri-bis derivative in acetone solution is heated for ten minutes with mercuric iodide. The pure product forms colourless crystals, but unless the experiment is performed in the dark only a red product is isolated.

5-Cyanomercuri-2:4-diphenyl-selenophene.—The 5-chloromercuri compound is treated with sodium cyanide in acetone solution. The mercuri-bis derivative is precipitated, and dilution of the filtrate gives a 50 per cent. yield of the 5-cyanomercuri compound, M.pt. 256·4° C. A 90 per cent. yield is obtained when the mercuri-bis derivative is heated for ten minutes in acetone solution with mercuric cyanide.

[1] Bogert and Herrera, *J. Amer. Chem. Soc.*, 1923, 45, 238; Bogert and Anderson *ibid.*, 1926, 48, 223.

DropBooks

When boiled in benzene, toluene, or xylene it is decomposed into 2 : 4-diphenyl-selenophene and mercurous cyanide.

Mercuri-bis-(2 : 4-diphenyl-selenophene-5), $(Ph_2C_4HSe)_2Hg$, may be isolated from the 5-chloromercuri compound and potassium bromide, sodium cyanide, or sodium iodide, also from the 5-bromomercuri compound and sodium bromide. It forms pale gray, minute, felted hairs, M.pt. 236·7° C. (corr.).

Derivatives containing mercury and arsenic are given under the latter element in Part II. of this volume.

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CHAPTER XI.

ORGANOMETALLIC DERIVATIVES OF THE METALS OF GROUP III.

Boron, aluminium, indium, and thallium are the only elements in this group from which true organo-compounds have been obtained. The metalloid boron forms a greater variety of compounds than the other three metals, its derivatives bearing some resemblance to those of silicon and phosphorus. Whilst aluminium and gallium when heated with dry hydrogen chloride yield $AlCl_3$ and $GaCl_3$ respectively, indium and thallium only give $InCl_2$ and TlCl respectively; also the stability of the trichlorides of these metals diminishes from aluminium to thallium. This gradation in basicity is reflected in the organo-compounds, for whilst it is possible to obtain the type R_3M from aluminium, only the form R_2MX can be isolated from indium and thallium. Moreover, in the case of the latter metal, the inorganic tervalent compounds are less stable than the thallous salts, but no organo-thallous derivatives have ever been isolated.

The first organic compound of boron was isolated by Frankland in 1862, by the interaction of zinc methyl and triethyl borate.[1] This method and the use of zinc alkyls with boron trichloride was continued until the discovery of the Grignard reagent. In 1909 [2] boron trimethyl was prepared by the action of magnesium methyl iodide on trimethyl borate, and in 1921 [3] a number of boron trialkyls were obtained by the interaction of magnesium alkyl halides and boron trifluoride. Of the derivatives of the type R_3B, boron trimethyl is a gas, spontaneously inflammable in air; boron triethyl, a spontaneously inflammable liquid; whilst the higher members of the series are liquids, readily oxidised when exposed to air. The methyl and ethyl derivatives combine with ammonia to form R_3B,NH_3. The type R_2BOH only has one representative, the ethyl compound, which is a liquid readily absorbing oxygen from the air.

The alkyl boric acids, $RB(OH)_2$, are best prepared by the action of magnesium alkyl halides on boric esters. They are all solids, and the lower members of the series are volatile at low temperatures.

In the aromatic series only one member has been obtained of the type R_3B, namely, boron triphenyl.[4] It is formed by the interaction of magnesium phenyl bromide and boron trifluoride, an excess of Grignard reagent giving boron diphenyl fluoride and boron phenyl difluoride at the same time. Boron triphenyl is a solid, which readily yields additive

[1] Frankland, *Annalen*, 1862, 124, 129.
[2] Khotinsky and Melamed, *Ber.*, 1909, 42, 3090.
[3] Krause and Nitsche, *Ber.*, 1921, 54, [B], 2784.
[4] Krause and Nitsche, *Ber.*, 1922, 55, [B], 1261.

compounds with ammonia and aromatic amines, in which boron has the co-ordination number 4.

The type R_2BX is represented by boron diphenyl chloride and bromide, both being prepared by the use of mercury diphenyl. The chloride is a liquid, B.pt. 270° to 271° C., and the bromide a solid, M.pt. 24° to 25° C. Treatment with sodium hydroxide yields the type $R_2B.OH$.

A considerable number of derivatives are known of the type RBX_2, the general method of preparation consisting of treating boron trichloride with mercury diaryls, in the proportion of 1 mol. of the latter to 2 mols. of the boron halide. Some of the products are solids, others fuming liquids, but all when treated with water are converted into the corresponding acids, $RB(OH)_2$.

The diaryl boric acids, $R_2B(OH)$, are confined to the diphenyl and di-p-tolyl compounds, although in the latter case the anhydride and not the acid is formed.

The monoaryl boric acids, $RB(OH)_2$, are usually isolated, as stated above, by the action of water on the type RBX_2, although in certain cases this leads to the formation of the oxide RBO. The phenyl compound has been obtained by boiling with water the product of reaction from magnesium phenyl bromide and boron trifluoride. The most remarkable feature of the type $RB(OH)_2$ is that the action of mercuric chloride upon them leads to the production of mercury aryl halides (RHgX). The anisyl and phenetyl compounds do not yield oxides when heated, or form salts, and the β-naphthyl acid exists in two modifications. Dehydration of the acids *in vacuo* gives the oxides, RBO.

Aluminium compounds of the type R_3Al were first investigated by Cahours in 1860.[1] They are difficult to handle, and the methyl, ethyl, and propyl derivatives are liquids, spontaneously inflammable in air. In attempting to devise new methods for the preparation of these substances, Krause and Wendt[2] isolated the etherates, $4AlR_3.3EtO$, which are colourless, mobile liquids rapidly undergoing decomposition in the air, but do not inflame.

Only one compound of each of the types R_2AlX and $RAlX_2$ is known, namely, the ethyl derivative, and this in each case is spontaneously inflammable, although the etherates, like those above, do not exhibit this property.

The only other alkyl compounds known are derivatives of methylene iodide or bromide, aluminium powder reacting with these compounds to produce the type $CH_2{=}AlX$, which are heavy liquids.

Aluminium triphenyl is the sole aluminium aromatic organic compound. Like the corresponding alkyls, it forms an etherate, but its decomposition by air is not so rapid. Mercury diphenyl and aluminium in a nitrogen atmosphere at 140° C. produce the compound, with much evolution of heat, in a few seconds. Iodine decomposes it, with formation of aluminium iodide and iodobenzene.

The metal indium has so far only yielded one derivative, indium diphenyl chloride.[3] This was isolated by the interaction of mercury diphenyl and metallic indium in boiling xylene. It is an insoluble compound, not melting at 350° C. When metallic indium and mercury diphenyl are heated at 270° C. in a nitrogen atmosphere under reduced

[1] Cahours, *Annalen*, 1860, 114, 242.
[2] Krause and Wendt, *Ber.*, 1923, 56, [B], 466.
[3] Goddard, unpublished.

pressure, and the residue extracted with ether, a compound corresponding to C_8H_5InO,In_2O_3 is isolated from the solution.

The first organic thallium compound was obtained by Hansen,[1] by treating zinc diethyl with thallic chloride. Four years later Hartwig[2] prepared salts of the type R_2TlX. No further work was done upon the metal until 1904, when Meyer and Bertheim[3] isolated thallium dimethyl chloride by a reaction which may be expressed in a general form:

$$TlCl_3 + 2MgRCl = R_2TlCl + 2MgCl_2$$

The present authors have shown since that this reaction may be used to form any aliphatic or aromatic compound of thallium of the type R_2TlX.[4] If it is desired to prepare thallium compounds containing secondary radicles, an excess of Grignard reagent must not be used, or reduction takes place to metallic thallium.[5] When thallium dialkyl halides are treated with silver oxide, the halogen is split off and hydroxides formed. The solutions thus obtained are strongly basic, rapidly absorb carbon dioxide from the air, and when treated with acids, or compounds containing acid groupings, they yield salts. Thallium diethyl hydroxide has been isolated in the solid state, and with aqueous solutions of metallic salts it precipitates hydroxides. In the case of halides, cyanides, or thiocyanates in the aliphatic series, the following reaction with silver nitrate takes place quantitatively,

$$R_2TlX + AgNO_3 = AgX + R_2TlNO_3$$

and since the nitrate is soluble, this affords a method of estimating the acid radicle.[6] Although many double salts are found in inorganic chemistry containing thallium in the thallic state, very few are met with in organometallic derivatives. In spite of the fact that the authors have prepared considerable numbers of salts of the type R_2TlX, both in the aliphatic and aromatic series, only the following double compounds have been isolated: thallium dimethyl m-nitrophenoxide, $C_8H_{10}O_3NTl.C_6H_5O_3N$; thallium diethyl 4-nitrosophenoxide, $C_{10}H_{14}O_2NTl.C_6H_4O_2N$; thallium diethyl 5-nitro-o-tolyloxide, $C_{11}H_{16}O_3NTl.C_7H_7O_3N$; thallium diphenyl acid propionate, acid valerate, acid butyrate, acid m-hexoate. Moreover, with the exception of the fluorides, none of the salts appear to contain water of crystallisation.

Thallium diphenyl bromide was first mentioned by Meyer and Bertheim in 1904, but in 1922 the present authors showed that this compound was impure, and that the reactions given for it did not represent the facts, as shown by their later preparation. They therefore claimed their preparation to be the first organometallic compound of thallium, in the aromatic series, to be obtained in the pure state. The compound, which is typical of the aromatic thallium diaryl halides, does not melt below 300° C., and may be crystallised from pyridine. The corresponding chloride is decomposed by iodine monochloride according to the equation:

$$Ph_2TlCl + 2ICl = 2PhCl + TlCl + I_2$$

[1] Hansen, *Ber.*, 1870, 3, 9.
[2] Hartwig, *Ber.*, 1874, 7, 298; *Annalen*, 1875, 176, 257.
[3] Meyer and Bertheim, *Ber.*, 1904, 37, 2051.
[4] Goddard and Goddard, *Trans. Chem. Soc.*, 1921, 119, 672, 1310; 1922, 121, 36, 256, 483; 1923, 123, 1161.
[5] Krause and Grosse, *Ber.*, 1925, 58, [B], 1933.
[6] Goddard, *Trans. Chem. Soc.*, 1921, 119, 673.

If the thallium diphenyl chloride be replaced by thallium diethyl bromide, only thallous iodide is isolated from the reaction. It has been pointed out that thallium dialkyl halides when treated with moist silver oxide yield the corresponding hydroxides, and that the latter with acids give salts. In the aromatic series, it is found that the best method of preparing the salts is to boil together a mixture of the halide, silver oxide, and the organic acid in toluene. Alcoholic potassium hydroxide transforms the halides to oxides, and these are also available for production of salts.

It is well known that many organo mercury compounds of the type R_2Hg react with metallic and non-metallic chlorides to form organometallic derivatives of the metals in question. The present authors [1] carried out a considerable number of reactions of this type, with various organometallic compounds, the results of which are shown in Table IV. of the Appendix.

It will be seen that a number of the reactions afford means of obtaining organo-thallium derivatives. In the case of organo compounds of the elements of Group V., it may be stated that phosphorus and antimony chlorides yield no organo-thallium derivatives, whereas arsenic and bismuth chlorides are capable of yielding compounds of the type R_2TlX.

Summarising the results for tin and lead compounds in the aliphatic and aromatic series, substances of the type R_4M give rise to R_2MX_2 and R_2TlX; R_3MX and R_3MR' yield thallous chloride and R_2MR_2 and R_3MX respectively; R_2MR_2' produces $R_2'MX_2$ and R_2TlX, where R' is the radicle of lower molecular weight; and R_2MX_2 merely exchanges its halogen, X_2, should it be bromine or iodine, for the chlorine of the thallic chloride.

Whilst 2-chloromercuri-thiophene and mercury 2 : 2'-dithienyl form organo derivatives when treated with arsenic trichloride,[2] thallic chloride merely decomposes the first compound, and gives no organic compound with the second. 2-Iodomercurithiophene is converted to 2-chloromercuri-thiophene and thallous chloride is formed. p-Aminophenylmercuric acetate treated with ethereal thallic chloride gives an unstable additive compound, corresponding to the formula, $2C_8H_9O_2NHg.TlCl_3$, and p-aminophenylmercuric chloride behaves similarly, but when the solutions are heated complete decomposition takes place. p-Bis-mercurianiline and sodio-camphor do not yield thallium derivatives under the above conditions. It is therefore evident that only normal compounds of the type R_2Hg give rise to thallium derivatives, where R may be any radicle except benzyl, thienyl, or an iso-group; in other cases substances of the type R_2TlX are formed.

The estimation of thallium [3] in organic compounds is carried out in a spherical flask of 200 c.c. capacity, having a short, ground-glass neck, carrying an air condenser 3 feet long. About 0·2 gram of substance is treated in the apparatus with 20 c.c. of fuming nitric acid, and the whole boiled until colourless. The contents of the flask are then rinsed out and evaporated to dryness, the residue dissolved in water, a few drops of dilute ammonia added, and the thallium precipitated by

[1] Goddard, *Trans. Chem. Soc.*, 1922, 121, 36; 1923, 123, 1161; Goddard and Goddard' *ibid.*, 1922, 121, 256, 482.

[2] Steinkopf and Bauermeister, *Annalen*, 1917, 413, 331.

[3] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 488.

hot potassium dichromate. In cases such as thallium diphenyl chromate, the thallium is first removed as thallous iodide, before precipitating the other metal. For halogen estimation, silver nitrate in 1 c.c. of water is added before the addition of the fuming nitric acid, and the mixture boiled to destroy organic matter, then treated in the usual way. This method of estimating halogens gives good results in the case of thallium, lead alkyl, and mercury compounds, and would no doubt answer for any type of organo compound which does not explode with fuming nitric acid, or give a stable nitrate, like lead diphenyl nitrate, or yield an insoluble oxide, as in the case of tin.

Boron.

Alkyl Compounds of the Type R_3B.

Boron trimethyl, Me_3B.—This compound was first obtained[1] by the interaction of zinc methyl and triethyl borate. It has more recently been prepared by the interaction of magnesium methyl iodide and trimethyl borate.[2]

The product isolated by the above methods is a gas of pungent odour, which is spontaneously inflammable in contact with air. Frankland states that it can be liquefied at 10° C., under a pressure of three atmospheres, to a colourless liquid, whilst Stock and Zeidler give the melting-point as −161·5° C. and the density at −100° C. as 0·625 (as liquid). They also recorded the following vapour pressures :—

Vap. press. in mm.	1	2	3	4	6	10	15	21
Temperature °C.	−118	−113	−108	−103	−98	−93·3	−88·4	−83·5

Vap. press. in mm.	32	43	60	82	113	147	192	253
Temperature °C.	−78·4	−73·8	−68·9	−64·1	−59·2	−54·3	−49·4	−44·5

Vap. press. in mm.	319	406	511	759
Temperature °C.	−39·6	−34·6	−29·7	−20·2

DropBooks

The vapour density between −25° C. and +100° C. corresponds to the formula BMe_3.

The gas is soluble with difficulty in water, but very easily soluble in alcohol and ether. It combines directly with ammonia, yielding *boron trimethylammine*, $BMe_3.NH_3$, M.pt. 56° C., B.pt. 110° C., which crystallises from ether in many-sided, highly refractive, volatile crystals. The compound has the vapour pressures 1·0 mm. at 0° C., 1·8 mm. at 5·6° C., 2 mm. at 10° C., 3·2 mm. at 15·2° C., 11·0 mm. at 31·2° C., and 16·5 mm. at 36·9° C. The vapour density, measured between 25·0° C. and 70·0° C., shows that about 10 per cent. of undissociated ammine can exist in the gaseous state at 25° to 30° C., but molecular weight determinations in benzene solution by the cryoscopic method show that the ammine is practically undissociated. The benzene solution is stable in air, smells faintly of boron trimethyl, but not of ammonia.

Treatment of boron trimethyl with potassium hydroxide or an ammoniacal solution with alcoholic potassium hydroxide yields a resinous mass, to which Frankland ascribed the composition $BMe_3.KOH$.

[1] Frankland, *Annalen*, 1862, 124, 129.

[2] Khotinsky and Melamed, *Ber.*, 1909, 42, 3090. A re-examination of Frankland's compound was made by Stock and Zeidler (*Ber.*, 1921, 54, [B], 531) who obtained the compound in the gaseous state from boron chloride and zinc methyl, the violence of the reaction being moderated by cooling or working under diminished pressure.

Boron triethyl.—This is prepared by the action of zinc ethyl on the triethyl ester of boric acid,[1] and also by the interaction of zinc ethyl and boron trichloride.[2] Frankland described it as a fuming liquid, spontaneously inflammable in air. It melts at −92·9° C., and boils at 95° C.; density at 23° C., 0·6931; vapour pressure at 0° C., 12·5 mm. It undergoes slow decomposition on heating, yielding some hydrogen and ethane: the vapour density near the boiling-point corresponds to the simple formula BEt_3.[3] The liquid is only very slightly soluble in water, prolonged treatment only showing very slow decomposition. Iodine has no action upon it even at 100° C. It burns in air with a bright green, sooty flame, and explodes in pure oxygen. When heated with concentrated hydrochloric acid over mercury to 99° C., an ethyl group appears to be replaced by halogen, yielding *boron diethyl chloride*. Like boron trimethyl, it forms an *ammine*, $BEt_3.NH_3$, which is stated to have an aromatic smell and an alkaline reaction.

Boron tri-n-propyl, $(C_3H_7)_3B$.[4]—This and the following trialkyl boron compounds are prepared by the action of boron fluoride on magnesium alkyl halides, details of a preparation being given under the isoamyl compound. The following physical data have been noted for the propyl compound: B.pt. 60° C. at 20 mm.; B.pt. 156° C. at 760 mm.; density at 24·7° C. 0·7204, whence density at 22·5° C. 0·7225; n_{H_α} 1·41129, n_D 1·41352, n_{H_β} 1·41895, n_{H_γ} 1·42354 at 22·5° C.

Boron tri-isobutyl, $(C_4H_9)_3B$.—B.pt. 86° C. at 20 mm. (uncorr.); B.pt. 188° C. at 760 mm.; density at 25° C. 0·7380, whence density at 22·8° C. 0·7400; n_{H_α} 1·41652, n_D 1·41882, n_{H_β} 1·42445, n_{H_γ} 1·42882 at 22·8° C.

Boron tri-iso-amyl $(C_5H_{11})_3B$.—Boron trifluoride obtained by the interaction of 75 grams of potassium borofluoride, 13 grams of boric anhydride, and 250 c.c. of concentrated sulphuric acid, is passed in a rapid stream into the magnesium compound from 106 grams (1 mol.) of isoamyl chloride in 350 c.c. of absolute ether. The boron trifluoride is rapidly absorbed, and after completion of the reaction the whole is heated to boiling for twenty minutes on the water-bath. The ether is then distilled off in a stream of nitrogen and the residue distilled in dry nitrogen at 13 mm. The pure product obtained distils at 119° C. at 14 mm. in nitrogen. Yield 42 grams (55 per cent.).

The compound is a colourless, very mobile liquid, having an odour resembling amyl alcohol. It is readily oxidised in air, yielding isoamyl boric acid. It burns with a bright green flame and is slowly acted upon by water.

Physical data: density at 23·4° C. 0·7600, whence density at 22·6° C. 0·7607; n_{H_α} 1·42983, n_D 1·43207, n_{H_β} 1·43782, n_{H_γ} 1·44254 at 22·6° C.

Alkyl Compounds of the Type $R_2B.OH$,

Boron diethyl hydroxide or Diethyl boric acid, $Et_2B.OH$,[5] is prepared by the action of water on the ethyl ester of diethyl boric acid. It is a liquid which cannot be distilled without decomposition; it

[1] Frankland, *Annalen*, 1862, 124, 129.
[2] Stock and Zeidler, *Ber.*, 1921, 54. [B], 531; Frankland, *Jahresber.*, 1876, p. 469.
[3] Stock and Zeidler, *loc. cit.*
[4] Krause and Nitsche, *Ber.*, 1921, 54, [B], 2784.
[5] Frankland, *loc. cit.*

absorbs oxygen from the air, forming the monoethyl ester of ethyl boric acid, EtB(OH).OEt. The O-ethyl derivative of the above compound, the *ethylate* of diethyl boric acid, Et_2.B.OEt, is prepared from the compound of the diethyl ester of ethyl boric acid with the triethyl ester of boric acid, Et.$B(OEt)_2$.$B(OEt)_3$, and zinc ethyl. The product is a colourless liquid, B.pt. 102° to 103° C., which is transformed by dry oxygen into the diethyl ester of ethyl boric acid, and is decomposed by water into alcohol and diethyl boric acid.

Alkyl Compounds of the Type RB.$(OH)_2$.

Methyl boric acid, Me.$B(OH)_2$.—Boric esters are best prepared by the action of alcohols on boric anhydride under pressure, and it has been found [1] that these esters react with Grignard's reagents to form the above type of compound, according to the equation:

$$RMgX+B(OR')_3=BR(OR')_2+R'O.MgX$$

The interaction of trimethyl boric ester and magnesium methyl iodide in ether, followed by decomposition with acidified water, yields methyl boric acid, as white crystals, very volatile and unstable. It has never been isolated in the pure state, but Michaelis and Becker [2] showed that it exerts a methylating action on magnesium phenyl bromide, the products consisting of phenyl boric acid and toluene. The esters of this acid are readily hydrolysed by cold water.

Ethyl boric acid, $EtB(OH)_2$, is deposited in white crystals from ether, readily subliming at 40° C., and very volatile. It may be prepared as the above methyl compound, or by decomposition of the diethyl ester of ethyl boric acid with water,[3] also by the action of water on the double compound of the diethyl ester of ethyl boric acid with triethyl boric acid. The acid is easily soluble in water, alcohol, or ether, has an acid reaction, but does not combine with bases.

The *monoethyl ester*, Et.B(OH)OEt, is a crystalline product, decomposed by water into alcohol and ethyl boric acid, and is prepared by the action of atmospheric oxygen on diethyl boric acid below 8° C.

The *diethyl ester*, Et.$B(OEt)_2$, is a liquid, boiling with decomposition at 125° C., and is decomposed by water like the monoethyl derivative. It is formed when boron triethyl is oxidised in air and then in oxygen, or when dry oxygen acts upon the ethyl ester of diethyl boric acid.

The ester combines with triethyl boric ester to form Et.$B(OEt)_2$.$B(OEt)_3$, which *compound* may also be obtained from zinc ethyl and 2 mols. of triethyl boric ester. It is a liquid, B.pt. 112° C., yielding ethyl boric acid, boric acid, and alcohol when treated with water, whilst zinc ethyl transforms it into the ethyl ester of diethyl boric acid.[4]

Propyl boric acid, C_3H_7.$B(OH)_2$, is described by Khotinsky and Melamed as melting at 74° to 75° C. and soluble in alcohol and ether. Krause and Nitsche,[5] however, prepared the compound by placing boron tripropyl in a flask filled with nitrogen, loosely corking the flask so that

[1] Khotinsky and Melamed, *Ber.*, 1909, 42, 3090.
[2] Michaelis and Becker, *Ber.*, 1880, 13, 58.
[3] Frankland, *Annalen*, 1862, 124, 40; *Jahresber.*, 1876, p. 468.
[4] Frankland, *ibid.*
[5] Krause and Nitsche, *Ber.*, 1921, 54, [B], 2784.

air could gradually diffuse in, when boron propyl oxide was obtained by oxidation, and this substance when recrystallised from a little hot water gave the required acid. It formed thick, colourless plates, M.pt. 107° C., easily soluble in hot water, with difficulty in cold water, and fairly soluble in the usual organic solvents.

Isobutyl boric acid, $(C_4H_9)B(OH)_2$, is prepared as above as colourless plates from hot water, M.pt. 112° C.[1]

Isoamyl boric acid, $(C_5H_{11})B(OH)_2$, forms colourless, rectangular plates from water, M.pt. 169° C. It is fairly soluble in the usual organic solvents, and forms sodium and ammonium salts, the latter being unstable and readily evolving ammonia.

Aryl Compounds of the Type R_3B.

Boron triphenyl, Ph_3B,[2] is prepared as follows: One quarter of the Grignard reagent from 156 grams of bromobenzene and 24 grams of magnesium in 500 c.c. of ether is saturated with the boron trifluoride from 52 grams of potassium borofluoride, 8 grams of boron trioxide, and 100 c.c. of concentrated sulphuric acid. The gas is readily absorbed, and afterwards the remainder of the Grignard reagent is added, the mixture being cooled in ice. The reaction is very violent, and the boron phenyl fluoride is transformed to boron triphenyl, this change being completed by several hours' heating on the water-bath. The ether is then distilled off, and the residue distilled in nitrogen at 13 to 15 mm. pressure in an oil-bath. Boron triphenyl slowly distils at 245° to 250° C. as a thick oil, which solidifies on cooling to colourless, thick, six-sided columns, some one centimetre in length. After several distillations in carbon dioxide it boils at 203° C. at 15 mm., M.pt. 136° C., the yield of pure product being about 50 per cent. of the theory.

The crystals resemble those of triphenylarsine and triphenylstibine in form, are easily soluble in benzene, toluene, and other benzene hydrocarbons, less soluble in ether, but react with alcohols forming esters. Its ethereal solution in the presence of sodium wire becomes intensely coloured, and deposits orange-yellow, prismatic crystals, but oxygen destroys the colour.[3, 4]

Boron triphenyl unites readily with ammonia and amines, yielding additive compounds in which boron has the co-ordination number 4. The method of preparation is general and consists in bringing the components together in ethereal solution.[5]

Boron triphenyl-ammonia, $Ph_3B.NH_3$, forms snow-white crystals, very difficultly soluble in ether or cold benzene, easily in hot benzene, cold methyl or ethyl alcohol. The crystals in the dry state are stable in air, begin to soften about 203° C., and melt with gas evolution to a clear, yellow-brown liquid above 212° C.

Boron triphenyl-methylamine, $Ph_3B.MeNH_2$, occurs as colourless prisms, having similar properties to the above compound. It sinters at 208° to 209° C., melting to a clear liquid at 210° to 211° C.

Boron triphenyl-ethylamine, M.pt. 166° to 168° C., and the corre-

[1] Khotinsky gives the melting-point as 104° C. and isoamyl boric acid as 101° C.
[2] Krause and Nitsche, *Ber.*, 1922, 55, [B], 1261.
[3] Krause, *Ber.*, 1924, 50, [B], 216.
[4] If excess of Grignard reagent is used in the above reaction, a mixture of boron triphenyl, boron diphenyl fluoride, and phenyl boron difluoride, appears to be formed.
[5] Krause, *Ber.*, 1924, 57, [B], 813.

sponding *n-propylamine* derivative melting above 180° C., with decomposition, have been prepared.

The *dimethyl* and *trimethylamine* derivatives melt at 200° C. and 135° to 137° C. respectively.

From aromatic compounds, the following combinations have been isolated: *boron triphenyl aniline*, M.pt. 138° to 140° C. with decomposition; with *pyridine*, M.pt. above 214° C. with decomposition; with *quinoline*, M.pt. 160° to 170° C. with decomposition; with *quinaldine*, M.pt. 110° to 112° C. with decomposition; with *piperidine*, M.pt. 213° to 214° C., decomposing above 216° C.; with *phenyl hydrazine*, M.pt. 138° to 140° C.

Aryl Compounds of the Type R_2BX.

Boron diphenyl chloride, Ph_2BCl, is a colourless liquid, faintly fuming in air, and slowly decomposed by water.[1] It is obtained by heating boron phenyl dichloride (8 grams) and 18 grams of mercury diphenyl in a sealed tube at 300° to 320° C. for twenty-four hours. The crude product is taken up in petroleum ether, the solvent removed, and the residue fractionated, the portion distilling at 270° to 271° C. being pure boron diphenyl chloride. Yield 3·5 grams.

Boron diphenyl bromide was first obtained as a by-product in the preparation of boron phenyl dibromide, from boron tribromide and mercury diphenyl, the compound being contained in the fraction distilling above 150° C. at 20 mm. It may be more readily isolated by taking the proportions represented by the following equation :—

$$Ph_2Hg + BBr_3 = Ph_2BBr + HgBr_2$$

A crystalline, colourless mass is formed, M.pt. 24° to 25° C., reddening in air, and decomposing with water with separation of diphenyl boric acid.[2]

DropBooks

Aryl Compounds of the Type RBX_2.

Boron phenyl difluoride, $Ph.BF_2$,[3] an oil, B.pt. 70° to 75° C.; difluoride has been previously mentioned under the preparation of boron triphenyl.

The *dichloride* is obtained according to the equation :

$$2BCl_3 + Ph_2Hg = 2PhBCl_2 + HgCl_2$$

the substances being heated in a sealed tube at 180° to 200° C. It is a colourless liquid, soon becoming red in air, and boiling at 175° C., although it may be solidified at low temperatures, but melts again at 0° C. Atmospheric moisture causes it to fume, and when dropped into water it is decomposed with a hissing noise. If chlorine is passed into the liquid at the ordinary temperature it is partly decomposed, yielding chlorobenzene and boron trichloride, but if all the air is removed by carbon dioxide before the chlorine is passed in boron phenyl tetrachloride results.

The dichloride reacts[4] with chlorobenzene and sodium to form boron triphenyl.

[1] Michaelis, *Ber.*, 1894, *27*, 244.
[2] Michaelis and Richter, *Annalen*, 1901, *315*, 26.
[3] Krause, German Patent, 371467; *Chem. Zentr.*, 1923, ii, 1089.
[4] Michaelis, *Ber.*, 1889, *22*, 241.

The *dibromide* is obtained when the boron trichloride in the above equation is replaced by the tribromide. It crystallises in colourless tablets, M.pt. 32° to 34° C., B.pt. 99° to 101° C. at 20 mm., fumes strongly in air, has a pungent smell, and is decomposed by water giving phenyl boric acid.

Boron o-tolyl dichloride is a colourless, thick oil having a strong smell, and faintly fuming in air. When cooled to 0° C. it solidifies, melting again at 6° C., and with water yields the corresponding boric acid.[1]

Boron p-tolyl difluoride,[2] is an oil, B.pt. 95° to 97° C. The corresponding *dibromide*[3] forms a white, crystalline mass, M.pt. 44° to 45° C., B.pt. 145° C. at 25 mm. (approx.), which fumes strongly in air, and is violently decomposed to the acid by water.

Boron o- and p-anisyl dichlorides, $CH_3O.C_6H_4.BCl_2$. The former was not analysed by Michaelis, but he stated that its properties were similar to those of the p-anisyl derivative. This latter compound is a light, yellowish-red to violet liquid, B.pt. 182° C. at 170 mm., and on cooling solidifies to a crystalline mass which melts at 30° C. It fumes strongly in air, and reacts vigorously with water to form the acid.

Boron o- and p-phenetyl dichlorides.—The first of these compounds has only been obtained in small quantities and has not been analysed, although the acid has been derived from it. The para compound is a colourless liquid, B.pt. 220° C. at 400 mm., which may be obtained as a crystalline mass, M.pt. 2° C., the general properties being similar to those of the anisyl derivative.

Boron o-xylyl dichloride boils at 212° C. and melts at about 0° C.[4] The *meta* compound is a colourless, very strongly fuming liquid, B.pt. 218° C., and is prepared by heating mercury di-m-xylyl with an excess of boron trichloride in a sealed tube at 200° C. for twenty-four hours.

Boron m-xylyl dibromide is a colourless, refractive liquid, boiling at about 125° C. at 15 mm., density at 15° C. 1·57.

Boron-p-xylyl dichloride may be prepared similarly to the meta compound, but the reaction takes place at 180° C. It distils as a transparent liquid at 205° C., and fumes strongly in air.

Boron pseudocumyl dibromide[5] is a colourless liquid, boiling between 170° and 190° C. at 16 mm., with partial decomposition. When treated with water it yields the oxide.

Boron α-naphthyl dichloride, $C_{10}H_7BCl_2$, boiling at about 164° C. at 25 mm., is prepared by heating mercury di-α-naphthyl and boron trichloride at 120° to 150° for eleven hours. The *β-naphthyl* derivative forms colourless needles, M.pt. 116° C., and is readily soluble in dry benzene, ether, or petroleum ether, fumes slightly in air, and yields the acid with water.

Aryl Compounds of the Type R_2BOH.

Diphenyl boric acid, $Ph_2B.OH$.[6]—When boron diphenyl chloride or bromide is treated with sodium hydroxide, and the clear solution

[1] Michaelis, *Ber.*, 1889, 22, 241; Michaelis and Becker, *ibid.*, 1879, 12, 58.
[2] Krause, German Patent, 371467; *Chem. Zentr.*, 1923, ii. 1089.
[3] Michaelis and Richter, *Annalen*, 1901, 315, 26.
[4] Michaelis, *Annalen*, 1901, 315, 19.
[5] $C_6H_2.Me.Me.Me.BBr_2$=1 : 2 : 4 : 5.
[6] Michaelis, *Ber.*, 1894, 27, 244; Michaelis and Richter, *loc. cit.*

neutralised with hydrochloric acid, the acid is formed, and may be extracted with ether. Evaporation of the solvent yields a fuming residue, B.pt. 215° to 235° C. at 17 mm., which crystallises on cooling; the crystals colour the flame green, and melt to a colourless liquid with hot water. It is soluble in the usual organic solvents and in alkalies, readily forming salts in the latter.

Di-p-tolyl boric acid is only known in the form of its *anhydride* $(CH_3.C_6H_4.B)_2O$, since the chloride has not been isolated in the pure state. This oxide is a white powder, M.pt. 78° C., easily soluble in organic solvents, but insoluble in water.

Aryl Compounds of the Types $RB(OH)_2$ *and* RBO.

Phenyl boric acid, $PhB(OH)_2$.[1]—The magnesium compound from 50 grams of bromobenzene in 200 c.c. of ether is saturated with the boron trifluoride from 52 grams of potassium borofluoride, 8 grams of boron trioxide, and 100 c.c. of concentrated sulphuric acid. After boiling for two hours under reflux, the product is ice cooled, and decomposed by cautiously adding 60 c.c. of water. The ether layer is then separated off, and the residue extracted several times with ether, the solvent removed, and the solid obtained boiled with 100 c.c. of water for one hour on the water-bath and filtered whilst hot. On slowly cooling, pure phenyl boric acid separates in snow-white bushy needles, several centimetres in length, M.pt. 216° C. It has similar properties to the compound obtained by Michaelis and Richter[2] by the action of water on boron phenyl dibromide. When kept *in vacuo* over phosphorus pentoxide it slowly changes to phenyl boron oxide. The *isobutyl ester* is a liquid, B.pt. 180° to 187° C. at 30 to 35 mm.

p-Chlorophenyl boric acid forms sheafs of needles, M.pt. 275° C., and **p-bromophenyl boric acid,** needles, M.pt. 191° C.

The following boric acids, unless otherwise stated, have been prepared by the action of water on compounds of the type $ArBX_2$:—[3]

o-Tolyl boric acid occurs as needles, M.pt. 160° to 161° C., easily soluble in alcohol or ether, but with difficulty in petroleum ether or water. When treated with ammoniacal silver solutions it gives a pale yellow, flocculent precipitate, which soon blackens on boiling, silver oxide and toluene being produced:

$$2C_7H_7BO_2HAg+3H_2O=2C_7H_8+2B(OH)_3+Ag_2O$$

With mercuric chloride, o-tolyl mercuric chloride is formed:

$$C_7H_7.B.(OH)_2+HgCl_2+H_2O=C_7H_7HgCl+HCl+B(OH)_3$$

m-Tolyl boric acid, M.pt. 137° to 140° C., reacts with mercuric chloride, yielding m-tolyl mercuric chloride. Its *isobutyl ester,* $C_6H_4.CH_3B(O.C_4H_9)_2$, is a liquid, B.pt. 195° to 207° C. at 66 mm., and it may be prepared by the following general reaction:—

$$RMgX+B(OR')_3=BR(OR')_2+R'O.MgX$$

which is carried out under pressure.[4]

[1] Krause and Nitsche, *Ber.*, 1922, 55, [B], 1261; Krause, German Patent, 371467; *Chem. Zentr.*, 1923, ii. 1089.

[2] Michaelis, *Ber.*, 1894, *27*, 244.

[3] Michaelis, *ibid.*

[4] Khotinsky and Melamed, *Ber.*, 1909, *42*, 3090.

p-Tolyl boric acid, M.pt. 240° C., yields p-tolyl mercuric chloride by the usual treatment. An alkaline solution of potassium permanganate oxidises the methyl group to carboxyl, when *p-carboxy-phenyl boric acid* is formed, $HOOC.C_6H_4.B(OH)_2$, as white, glistening, refractive needles, M.pt. 225° C. The crystals are easily soluble in hot water or alcohol, less soluble in ether or benzene, and when heated no anhydride is formed. Rapid heating decomposes the compound to benzoic acid and meta-boric acid:

$$C_6H_4\begin{cases}COOH\\B(OH)_2\end{cases} = C_6H_5COOH + BO(OH)$$

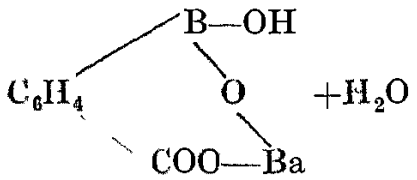
this reaction being similar to that of the related phosphorus derivative, namely:

$$C_6H_4\begin{cases}COOH\\PO(OH)_2\end{cases} = C_6H_5COOH + HPO_3$$

The reaction with mercuric chloride takes a somewhat different course in the case of this compound:

$$C_6H_4\begin{cases}COOH\\B(OH)_2\end{cases} + HgCl_2 + H_2O = C_6H_4\begin{cases}COOH\\HgCl\end{cases} + HCl + B(OH)_3$$

This chloromercuri benzoic acid is a white, crystalline powder, M.pt. 272° C., soluble in absolute alcohol and insoluble in water, dissolves in aqueous alkalies, but is reprecipitated by acids. The *barium* salt of p-carboxy-phenyl boric acid,



is obtained as a white precipitate by the action of barium chloride on a carbon dioxide-free, ammoniacal solution of the acid. It is very soluble in cold water, but the solubility diminishes with rise of temperature. At 200° C. the water of crystallisation is not driven off, and the hydroxyl group bound to the boron atom is unaffected.

Two *lead* salts are known, both white powders, namely:

$$[HO(HOPbO)BC_6H_4COO]_2Pb \text{ and } (PbO_2B.C_6H_4COO)_2Pb.2H_2O$$

The *silver* salt, $AgO.CO.C_6H_4.B(OH)OAg$, is a white precipitate, easily decomposed, and yellow when dry. On heating with water it first becomes brown, then black, and silver oxide separates, along with boric and benzoic acids, or silver benzoate.

o-Anisyl boric acid occurs as small, glistening plates, from hot water, M.pt. 165° C.; the *para* acid yields white tablets of the monoclinic system, melting at 201° to 203° C., soluble in ether, hot alcohol, or benzene, less soluble in hot water. It reacts with ammoniacal silver solutions in the usual way, and yields p-anisylmercuric chloride with mercuric chloride.

o-Phenetyl boric acid crystallises from water in small, white

needles, M.pt. 171° C.; the *para* compound in clusters of feathery, glistening needles, M.pt. 159° C., which are easily soluble in cold alcohol, ether, or hot benzene. Both compounds react with mercuric chloride, but neither of them yields an oxide on heating, or forms salts, these properties being shared by the anisyl compounds.

Benzyl boric acid, M.pt. 161° C.,[1] forms an *isobutyl ester*, B.pt. 189° to 196° C. at 36 mm.

o-Xylyl boric acid[2] yields fine, colourless needles, M.pt. 190·5° C.; the *meta* acid is obtained by heating the oxide with water, its *diethyl ester* being a colourless liquid, B.pt. 160° C., formed when boron m-xylyl dichloride is dropped into a large excess of absolute alcohol. The *para* acid crystallises from water in feathery groups of hair-like needles, M.pt. 186° C., which slowly change to the oxide in the desiccator.

α-Naphthyl boric acid[3] crystallises in fine, colourless needles from water, sintering at 242° C. and melting at 259° C. It is easily soluble in ether, alcohol, hot water, with difficulty in petroleum ether or cold water. α-Naphthyl mercuric chloride may be isolated from the acid in the usual way. When boiled with water, particularly in the presence of alkali, the acid yields naphthalene and boric acid:

$$C_{10}H_7B(OH)_2+H_2O=C_{10}H_8+B(OH)_3$$

Although the acid reddens litmus, it only forms salts with difficulty; the *barium* and *silver* salts are known, the latter reacting with water to produce naphthalene, silver oxide, and boric acid.

β-Naphthyl boric acid exists in two modifications. When recrystallised from water, colourless plates are produced, melting at 248° C.; these when dissolved in a little alcohol, and the solution poured into cold water, appear as the second modification, in fine needles, M.pt. 266° C.; recrystallisation from hot water changes this second form back into the first. The latter modification acts towards alkali and mercuric chloride as the α-naphthyl acid. The *barium* salt forms pale reddish plates, easily soluble in hot water, and the *silver* salt is also known. Distillation of boron-β-naphthyl dichloride and sodium methylate under 50 mm. pressure leads to the formation of the *methyl ester* of the acid, which is an odourless, thick, colourless liquid, boiling at 160° to 180° C. at 50 mm. It fumes in air, and changes to the oxide when treated with water.

The following oxides are formed either by the action of water on the dihalides or by dehydration of the acid *in vacuo*. Those obtained by the first method are marked (A), by the second (B).

Phenyl boron oxide, (A) and (B).

o-Tolyl boron oxide, (B), is a white powder, soluble with difficulty in alcohol or ether, and supposed to be formed when the acid melts. The corresponding *para* oxide, (B), melting at 257° to 258° C., is reconverted by hot water to the acid.

o-Xylyl boron oxide, (B), M.pt. 226° C.—The dehydration of the acid in this case only requires forty-eight hours, but in the case of p-xylyl boric acid three weeks is needed to complete the change.

m-Xylyl boron oxide, (A), crystallises from ether in white needles, M.pt. 202° C., is soluble in alcohol or benzene, but insoluble in cold water. A solution of the oxide in very dilute ammonium hydroxide, when treated

[1] Khotinsky and Melamed, *Ber.*, 1909, **42**, 3090; Krause, German Patent, 371467; *Chem. Zentr.*, 1923, ii. 1089.

[2] Michaelis, *Annalen*, 1901, **315**, 19. [3] Michaelis, *Ber.*, 1894, **27**, 244.

with silver nitrate, gives a pale yellow precipitate of the *acid silver salt*, $C_8H_9B(OH)(OAg)$.

p-Xylyl boron oxide, (B), M.pt. 176° C., forms a *silver* salt as above.

Pseudocumyl boron oxide, (A), crystallises from ether in white, glistening needles, M.pt. 211° C., insoluble in water, easily soluble in the usual organic solvents.

α-Naphthyl boron oxide is a white, micro-crystalline powder, difficultly soluble in ether or petroleum ether, but more soluble in alcohol.

β-Naphthyl boron oxide, (B), may be prepared also by the action of sodium ethoxide upon boron naphthyl dichloride:

$$C_{10}H_7BCl_2 + 2NaOEt = C_{10}H_7BO + 2NaCl + Et_2O$$

The oxide crystallises in fine, colourless needles, M.pt. 266° C., is soluble in alcohol, with difficulty in ether, and insoluble in light petroleum. It requires prolonged boiling with water to change it back to the acid.

Aluminium.

Alkyl Compounds of the Type R_3Al.

Aluminium trimethyl, Me_3Al, is a fuming liquid, spontaneously inflammable in air, solidifying to a crystalline mass about 0° C. It was no doubt obtained for the first time by Cahours,[1] but only in small quantities, by the action of mercury dimethyl upon aluminium at 100° to 130° C. The work has been repeated,[2] the same components being heated for several hours in a sealed tube placed in a water-bath. The compound obtained is then distilled over fresh aluminium, and afterwards distilled in hydrogen, the liquid distilling at 130° C. The boiling-point[3] is 127° to 129° C., and vapour density determinations indicate that the substance has the simple formula, Me_3Al.[4]

Aluminium triethyl may be prepared in a similar manner to the methyl compound.[5] Aluminium triethyl is a liquid, B.pt. 194° C. when distilled in hydrogen; it does not solidify at −18° C. It is decomposed with explosive violence by water; with iodine it yields ethyl iodide and iodine derivatives. At 234° C. the vapour density is 4·5 (theory 3·9), the refractive index having the value n_D 1·480 at 6·5° C.

A *compound* of aluminium triethyl with aluminium bromide has also been described, $(C_2H_5)_3Al.AlBr_3$, but its existence seems doubtful.[6]

Aluminium tripropyl,[7] formed in the usual way at 130° C., is a

[1] Cahours, *Annalen*, 1860, 114, 242.

[2] Buckton and Odling, *Annalen, Supp.*, 1865–1866, 109–113; *Proc. Roy. Soc.*, 1865, 14, 19.

[3] Quincke, *Zeitsch. physikal. Chem.*, 1889, 3, 164.

[4] See Louise and Roux, *Compt. rend.*, 1888, 107, 601; *Bull. Soc. chim.*, 1888, [2], 50, 511. Buckton and Odling gave the following figures for the vapour density: 2·80 at 240° C.; 2·80 at 220° C.; and 2·81 at 220° C., theory requiring the value 2·5; the refractive index is n_D^{12} 1·432 (Bleekrode, *Rec. trav. chim.*, 1885, 4, 80).

[5] Cahours states that aluminium and ethyl iodide when heated in a sealed tube for 24 hours at 130° give rise to a colourless liquid, fuming in air and boiling at 340° to 350° C. It is found to be a double compound of aluminium iodide and aluminium triethyl, but treatment with zinc ethyl decomposes it with the formation of zinc iodide and aluminium triethyl. A similar observation was made by Hallwachs and Schafarik (*Annalen*, 1859, 109, 207), but these investigators only appear to have isolated the double compound.

[6] Fürstenhoff, *Chem. Zentr.*, 1904, i. 785.

[7] Cahours, *Jahresber.*, 1873, p. 518; *Ber.*, 1873, 6, 567; *Compt. rend.*, 1873, 76, 133, 748, 1383; Louise and Roux, *loc. cit.*

colourless liquid, inflammable in air, B.pt. 248° to 252° C. It yields with water, propane and aluminium hydroxide.

Aluminium tri-isobutyl [1] is a colourless liquid, fuming in air.

Aluminium tri-isoamyl is a liquid, boiling about 250° C. at 80 to 100 mm.; vapour density determinations indicate the formula to be $Al_2(C_5H_{11})_6$.[2]

Aluminium Triallkyl Etherates.[3]

Aluminium triethyl-etherate, $4AlEt_3$, $3Et_2O$, may be obtained in several ways, namely :

1. By the action of ethyl bromide on an alloy of magnesium and aluminium in the presence of dry ether. The alloy contains 15·16 per cent. of aluminium, 0·24 per cent. of silicon, and traces of iron and calcium. The reaction mixture is cooled, and the ethyl bromide added in small portions, as the reaction is vigorous. After completion, the ether is distilled off and the residue distilled in nitrogen under reduced pressure, namely, at 140° to 180° C. at 14 to 16 mm.
2. From aluminium triethyl and anhydrous ether.
3. In quantitative yield from ethyl magnesium bromide and anhydrous aluminium chloride.

The etherate is a colourless, mobile liquid, B.pt. 112° C. at 16 mm., and is stable in a sealed tube, even when exposed to light. It reacts with explosive violence with water, but is not spontaneously inflammable in air, although it undergoes rapid decomposition. At atmospheric pressure its boiling-point is 216° to 218° C., slight decomposition taking place. The following physical constants have been determined : B.pt. 110·5° C. at 13·5 mm.; density at 17·4° C., 0·8200 ; n_{H_α} 1·43433 ; n_D 1·43700 ; n_{H_β} 1·44349 ; n_{H_γ} 1·44884 at 17·4° C.

Aluminium trimethyl etherate, B.pt. 68° C. at 15 mm., tends to be spontaneously inflammable.

Aluminium tripropyl etherate, B.pt. 135° C. at 18 mm., fumes strongly in air.

Alkyl Compounds of the Types R_2AlX *and* $RAlX_2$.

Aluminium powder and dry ethyl iodide, free from alcohol, react in a nitrogen atmosphere to give a mixture of these types of compounds. In air, the compounds are spontaneously inflammable, but the etherates do not exhibit this property.[4] **Aluminium diethyl iodide** is a clear, mobile liquid, B.pt. 118° to 120° C. at 4 to 5 mm., density 1·609 at 27° C. **Aluminium ethyl di-iodide** has M.pt. 35° to 37° C., B.pt. 158° to 160° C. at 4 mm. When its ethereal solution is treated with benzoyl chloride, *aa*-dibenzoylethane, a little propiophenone and ethane are formed.[5] Acetone and acetophenone with aluminium ethyl or isoamyl iodides yield mesityl oxide and triphenylbenzene respectively.[6] The following *compounds* have also been obtained : $Al_2I_3(NH_2)_3.Et_2O$, from aluminium ethyl iodide and ammonia ; $Al_2I_3(NHEt)_3.Et_2O$, from aluminium propyl

[1] Cahours, *Compt. rend.*, 1873, 77, 1403.
[2] Louise and Roux, *loc. cit.*
[3] Krause and Wendt, *Ber.*, 1923, 56, [B], 466.
[4] Grignard and Jenkins, *Compt. rend.*, 1924, 179, 89.
[5] Leone, *Atti. R. Accad. Lincei*, 1925, [vi.], 1, 229, 443.
[6] Leone and Braicovie, *Atti. R. Accad. Lincei*, 1924, [v.], 33, 567.

Dropbooks

iodide and ethylamine; $Al_2I_3(NMe_2)_3.Et_2O$, from aluminium propyl iodide and dimethylamine; $Al_2I_3(NHPh)_3.Et_2O$, from aluminium ethyl iodide and aniline. All these compounds are white, crystalline powders, decomposed by moisture with evolution of ammonia.

Aluminium Compounds from Methylene Iodide.

When aluminium and methylene iodide are allowed to stand for a considerable period, a reaction takes place and the mixture solidifies. The compound is white, crystalline, and highly reactive.[1] If the reaction is allowed to take place in anhydrous ether, the aluminium dissolves, a heavy liquid is obtained, and ethylene evolved. The reaction is represented as taking place as follows :—

$$3CH_2I_2 + 4Al = 3CH_2 : AlI + AlI_3$$
$$6CH_2I_2 + 4Al = 3C_2H_4 + 4AlI_3$$

With methylene bromide a similar *compound* is obtained, but the reaction is slower and less ethylene is evolved. The compounds yield additive products with iodine, $CH_2I.AlBrI$, and the latter when decomposed by water gives methyl iodide:[2]

$$CH_2I.AlBrI + H_2O = CH_3I + AlBrI.OH.$$

Aryl Compounds of the Type R_3Al.

Aluminium triphenyl, Ph_3Al.[3]—Five grams of mercury diphenyl and 1 gram (4 mols.) of aluminium sheet cut into small pieces are heated in complete absence of air and moisture in a stream of hydrogen or nitrogen. At 140° C. the reaction takes place with considerable evolution of heat and goes quantitatively to completion in ten to fifteen seconds. The reaction mass contains some metallic mercury, amalgamated aluminium, and a faint yellow, viscous product, which crystallises on standing. It is washed with dry ether, in which the bulk dissolves leaving a small residue which is filtered off, and the ether is then removed *in vacuo*. The product thus obtained as fine, white needles, M.pt. 112° to 113° C., contains 1 mol. of ether of crystallisation ($Ph_3Al.Et_2O$); this on removal by heat gives pure aluminium triphenyl, M.pt. 196° to 200° C. In compact masses the decomposition by air is slow, but dry air passed through the ethereal solution produces a white, amorphous precipitate, probably phenyl aluminium oxide (PhAlO). With water the compound inflames, aluminium hydroxide, benzene, and diphenyl being formed. Its addition compound with ether is only stable in perfectly dry solvents. Aluminium triphenyl reacts with alcohol with evolution of heat, but the compound produced does not appear to be the alcoholate, but an infusible compound, which yields some benzene and a strong smell of phenol on treatment with water.

Condensation products formed by acetone and chloroform do not appear to have been very thoroughly investigated, but iodine decomposes aluminium triphenyl, yielding aluminium iodide and iodobenzene.

[1] Thomas, *Compt. rend.*, 1922, 174, 464.
[2] Faillebin, *Compt. rend.*, 1922, 174, 112.
[3] Hilpert and Grüttner, *Ber.*, 1912, 45, 2828.

Indium.[1]

Indium diphenyl chloride.—Indium trichloride [2] from 1·16 grams of metallic indium, and 10·77 grams of mercury diphenyl (3 mols.) are boiled with 50 c.c. of xylene for thirty-seven hours. After filtering, the residue mostly melts at 245° to 250° C., but a portion does not melt at 295° C. The mass is extracted in a Soxhlet apparatus with dry benzene to remove any mercury compounds, and the residue in the thimble (0·647 gram) is organic and found to be indium diphenyl chloride. It is a crystalline, cream-coloured powder, insoluble in the usual organic solvents, and does not melt at 350° C.

Indium phenyl oxide.—Metallic indium (1·5 grams) and 2·25 grams of mercury diphenyl are heated at 270° C. in a nitrogen atmosphere for thirty minutes, the operation being carried out at a pressure of 17·2 mm. After cooling, the product is extracted with dry ether and the solvent allowed to evaporate spontaneously. An oil remains which solidifies on the addition of light petroleum. This is taken up in ether and reprecipitated with light petroleum, when a cream-coloured organic compound is obtained. It does not melt at 290° C., and its composition corresponds to $C_6H_5InO.In_2O_3$. It is insoluble in cold benzene, and only sparingly soluble in cold glacial acetic acid.

Thallium.

Alkyl Derivatives of the Type R_2TlX.

DropBooks

Thallium dimethyl chloride, $(CH_3)_2TlCl$, is prepared by dissolving the sulphydrate in acetic acid, and after boiling to expel the hydrogen sulphide, dilute hydrochloric acid is added. On cooling, the chloride separates in glistening, white, shimmering plates, which do not decompose at 280° C.[3]

Thallium dimethyl bromide may be obtained by the interaction of magnesium methyl bromide and thallic chloride, and crystallises from dilute ammonia containing sodium bromide in white, silver, glistening plates, which do not melt at 275° C. When treated with silver fluoride it yields **thallium dimethyl fluoride,** which decomposes above 230° C. It forms a hydrate containing 12 mols. of water.[4]

Thallium dimethyl iodide.—This compound is obtained [5] by treating the mother-liquors from the above bromide with potassium iodide, the decomposition temperature of the product being given as 264° to 266° C. It may also be prepared by the action of magnesium methyl iodide on thallic chloride. Obtained in this manner it only shows

[1] Goddard, unpublished.

[2] In order to prepare this salt, metallic indium is placed in a porcelain boat in a combustion tube into which chlorine is passed, the other end of the tube being protected from moisture by means of a calcium chloride tube. When all the air has been displaced, the tube is carefully heated, the indium burning with a pale blue flame, and the trichloride subliming in white crystals along the tube. After cooling, the chlorine is replaced by nitrogen and the chloride washed into a flask with dry ether.

[3] Meyer and Bertheim, *Ber.*, 1904, 37, 2051.

[4] Krause and Grosse, *Ber.*, 1925, 58, [B], 272.

[5] Meyer and Bertheim, *loc. cit.*

slight decomposition at 295° C., and does not melt at 300° C.[1] The reaction takes place according to the equation :

$$TlCl_3 + 2MgRI = TlR_2I + MgCl_2 + MgClI$$

The iodide crystallises from hot water or dilute ammonium hydroxide in shining silvery plates, which are only slightly soluble in alcohol or acetone, and insoluble in ether or light petroleum.

Thallium dimethyl hydrosulphide.—When an excess of yellow ammonium sulphide is added to an ammoniacal solution of thallium dimethyl bromide, a white precipitate of the hydrosulphide separates. This is washed with hydrogen sulphide water to purify it, but it tends to form a colloidal solution, which is difficult to filter. When dry it decomposes with explosion on heating or in contact with fuming nitric acid. It dissolves in dilute nitric acid, with the separation of sulphur; and in dilute sulphuric or acetic acid, with the evolution of hydrogen sulphide.

Thallium dimethyl carbonate.—This compound crystallises in large, hexagonal plates from the solution occurring from the interaction of thallium dimethyl iodide and silver oxide, after boiling and evaporating in air, the hydroxide formed during the reaction absorbing carbon dioxide. It is very soluble in water, moderately so in alcohol or acetone, and slightly soluble in ether. By treatment with mineral acids carbon dioxide is evolved and salts are formed.

Thallium dimethyl nitrate is formed when silver nitrate and thallium dimethyl iodide are boiled together in aqueous solution. The salt does not melt at 300° C. and crystallises from alcohol in shining, white plates, which are soluble in water and acetone, but less soluble in ether.

Thallium dimethyl chromate is prepared as above, using silver chromate, and forms brilliant yellow plates from water, these decomposing at 255° C. without melting. The chromate is very soluble in water, alcohol, or acetone, and dissolves slightly in ether or light petroleum,

The following methyl compounds have been prepared by treating thallium dimethyl iodide with silver oxide, boiling the mixture until all the thallium compound has dissolved, and then adding to the solution of thallium dimethyl hydroxide thus obtained, the nitrophenol or nitrocresol, and evaporating the whole until crystals appear.[2]

Thallium dimethyl o-nitrophenoxide crystallises from water in brick-red needles, which melt at 237° C. It is easily soluble in warm alcohol or pyridine, moderately soluble in acetone, chloroform, or toluene, slightly soluble in ether or carbon tetrachloride, and insoluble in light petroleum.

Thallium dimethyl m-nitrophenoxide is isolated both as the *acid* and *normal* salt. The former has the formula, $C_8H_{10}O_3NTl.C_6H_5O_3N$, and crystallises from water in brilliant red cubes, which soften at 150° C., and melt to a clear red liquid at 159° C. The normal compound, however, crystallises in yellowish-orange plates, which melt to a red liquid at 202° C., the latter decomposing on boiling. This form may also be derived from the acid variety by treatment with alcohol or ether. It is soluble in cold pyridine, acetone or warm alcohol, moder-

[1] Goddard, *Trans. Chem. Soc.*, 1921, 119, 672.
[2] Goddard, *ibid.*, 1310.

ately soluble in ether, toluene, or chloroform, and insoluble in carbon tetrachloride or light petroleum.

Thallium dimethyl p-nitrophenoxide crystallises from alcohol in yellow plates, which darken at 273° C. and explode violently at 275° C. It is easily soluble in cold pyridine, moderately soluble in alcohol or acetone, and insoluble in other organic solvents.

Thallium dimethyl 4 : 6-dinitro-2-aminophenoxide.—This compound, which is obtained by the use of picramic acid, crystallises from water in small, deep reddish-violet plates, darkening at 220° C. and melting with decomposition at 236° C. It is easily soluble in alcohol, acetone, or pyridine, moderately soluble in ether, and insoluble in chloroform, carbon tetrachloride, toluene, or light petroleum.

Thallium dimethyl 3-nitro-o-tolyloxide crystallises in deep red plates, which have a brown reflex, and melt to a deep red liquid at 186·5° C. The salt is readily soluble in cold pyridine, warm alcohol, acetone, ether, toluene, or chloroform, moderately soluble in carbon tetrachloride, and slightly soluble in light petroleum. The colour of all these solutions is red, dilution not completely destroying the red tone.

Thallium dimethyl acetate is formed when thallium dimethyl hydroxide solution is treated with acetic acid, the concentrated solution yielding elongated plates, M.pt. 293° C. The acetate is very soluble in water, alcohol, or acetone, less soluble in ether or petroleum.

Thallium diethyl chloride.—This derivative was first obtained by the action of zinc diethyl on thallic chloride.[1] Hansen stated that his compound was soluble in hot water, alcohol, and ether, crystallised in silky, glistening crystals, which remained unmelted at 225° C., and decomposed with explosion on sudden heating, forming thallous chloride and a gas. The specimen obtained by Hartwig [2] was scarcely soluble in ether, and when heated in the dry state in a paraffin bath to 190° C. decomposed with slight explosion, an inflammable gas being evolved. Another preparation [3] from the interaction of magnesium ethyl chloride and thallic chloride was stated to decompose at 205° to 206° C., and to be more difficultly soluble than the methyl compound. The present author, however, from his observations of these thallium compounds, is inclined to believe that this chloride does not melt even at 300° C.

Thallium diethyl fluoride decomposes above 170° C. and forms a hydrate crystallising in plates.

Thallium diethyl bromide is easily isolated from magnesium ethyl bromide and thallic chloride; its solubility falls between that of the chloride and iodide, and it remains unmelted at 300° C.

Thallium diethyl iodide crystallises from water in white plates when quite pure, and investigators differ regarding its temperature of decomposition.[4] It may be prepared from the corresponding chloride or bromide by the addition of potassium iodide to their aqueous solutions, or by the interaction of thallium diethyl sulphate and barium iodide, also by use of the Grignard reagent. It is difficultly soluble in water, alcohol, or ammonia, but may easily be recrystallised from pyridine.

Thallium diethyl hydroxide.—All the above halide compounds when boiled with silver oxide give a solution of the hydroxide, and when

[1] Hansen, *Ber.*, 1870, 3, 9; Hartwig, *ibid.*, 1874, 7, 298.
[2] Hartwig, *Annalen*, 1875, 176, 257.
[3] Meyer and Bertheim, *Ber.*, 1904, 37, 2051.
[4] Hartwig gives 195° C.; Meyer and Bertheim, 185° to 187° C.; Goddard, above 300° C.

making salts such a solution may be used, since it is not necessary to isolate the solid hydroxide. This, however, may be accomplished as follows: 6·4 grams of thallium diethyl iodide are dissolved in 300 c.c. of boiling water, and the silver oxide derived from 20 grams of silver nitrate added, whilst the whole is kept boiling by leading in steam until a test portion of the filtrate is halogen-free. The liquid is then filtered in carbon dioxide-free air, and evaporated to a small bulk in a stream of hydrogen. After cooling in the gas stream, a white, crystalline mass appears, and this is dried *in vacuo* over phosphorus pentoxide and soda lime. The base thus obtained melts at 127° to 128° C., is very soluble in water and alcohol, the solutions acting strongly alkaline towards litmus, and rapidly absorbing carbon dioxide from the atmosphere. It explodes in contact with fuming nitric acid, precipitates the hydroxides of metals from their aqueous solutions, and yields salts when treated with acids or compounds containing acid groupings.

Thallium diethyl hydrosulphide is prepared in a like manner to the dimethyl compound and possesses similar properties.

Thallium diethyl carbonate.—When the corresponding bromide or iodide is boiled with silver oxide in aqueous solution, and the filtrate evaporated in the presence of air, the carbonate is deposited in glistening needles, which decompose at 204° C. The salt may be recrystallised from alcohol, or precipitated from alcoholic solution by ether, and it is less soluble in hot water than in cold. Its solutions show an alkaline reaction, and when treated with acids, salts are formed with the evolution of carbon dioxide.

Thallium diethyl hydrogen carbonate.—When the above salt is dissolved in water and the solution saturated with carbon dioxide, the addition of alcohol precipitates the hydrogen carbonate as a white, crystalline powder. This in solution reacts feebly alkaline, but if the solution be evaporated by heating, the normal salt is again formed.

Thallium diethyl nitrite.[1]—A suspension of thallium diethyl iodide in acetone is shaken with the calculated amount of silver nitrite for one hour, and allowed to stand overnight. After filtration, the acetone solution is evaporated, the nitrite crystallising in large transparent plates, which remain unmelted at 290° C. It is also completely soluble in hot pyridine, but insoluble in other organic solvents.

Thallium diethyl nitrate.—When the aqueous solution derived from the interaction of thallium diethyl chloride and silver nitrate is concentrated, white plates are deposited. This compound, which is the nitrate, is said by Hartwig to explode at 236° C., but this seems doubtful, considering that the nitrite does not decompose at 300° C. The compound is moderately soluble in water, with difficulty in alcohol, and insoluble in ether.

Thallium diethyl sulphate may be prepared by the same method as the nitrate, and crystallises in plates or needles, which are stated to explode above 205° C. It is soluble in water, ether, or alcohol.

Thallium diethyl phosphate crystallises in needles, exploding at 189° C. and easily soluble in water and alcohol, slightly soluble in ether.

Thallium diethyl chromate is deposited from aqueous solution in brilliant yellow plates, which are also very soluble in alcohol, but less so in ether. The chromate decomposes with violent explosion at 193° C.

Thallium diethyl thiocyanate forms small, colourless plates,

[1] Goddard, *Trans. Chem. Soc.*, 1922, 121, 37.

which are readily soluble in water or alcohol, but only slightly so in ether. The compound is quite stable up to 300° C.

Whilst the foregoing compounds were prepared by the action of silver salts on thallium diethyl halides, those now to be described were obtained by direct action of acid compounds on thallium diethyl hydroxide solutions.[1]

Thallium diethyl acetate crystallises in short white needles, M.pt. 232° to 233° C., and has a similar solubility to the corresponding methyl compound. Hartwig described an acetate which slightly blackened at 212° C., and distilled unchanged at 245° C.

Thallium diethyl trichloroacetate forms white, crystalline plates, which do not melt at 300° C. The salt is very soluble in water, alcohol, or acetone, but less so in light petroleum.

Thallium diethyl propionate, M.pt. 228° to 229° C., occurs in fine, short needles, completely soluble in hot alcohol, ethyl acetate, toluene, or acetone, in cold pyridine or chloroform, moderately soluble in hot ether or carbon tetrachloride, and slightly soluble in light petroleum.

Thallium diethyl valerate yields small needles, M.pt. 215° C., which are completely soluble in cold alcohol, ether, pyridine, chloroform, or hot carbon tetrachloride, moderately soluble in cold toluene, acetone, or ethyl acetate, and insoluble in light petroleum.

Thallium diethyl n-hexoate forms transparent needles, half an inch in length, softening at 182° C. and melting at 190° C.; except for its solubility in light petroleum, it agrees in all respects with the valerate.

Thallium diethyl n-octoate occurs as long, transparent needles, M.pt. 159° C., which exhibit similar solubility to the hexoate.

Thallium diethyl lactate crystallises in small plates from alcohol, which decompose suddenly without melting at 267·5° C. The salt is soluble in cold water, acetone, or alcohol, and easily soluble in boiling chloroform, toluene, or ethyl acetate.

Thallium diethyl p-nitrobenzoate yields microscopic needles, M.pt. 213° C., which are completely soluble in cold pyridine, moderately soluble in alcohol or chloroform, slightly soluble in carbon tetrachloride, toluene, ethyl acetate, or acetone, and insoluble in ether or light petroleum.

Thallium diethyl p-iodobenzoate forms small white needles, decomposing with slight explosion at 220° C. and having a similar solubility to the p-nitrobenzoate.

Thallium diethyl m-bromobenzoate yields small, white needles, which decompose with considerable gas evolution at 220° C., and with the exception of its insolubility in acetone, the compound resembles the nitrobenzoate.

Thallium diethyl o-nitrophenoxide softens at 200° C. and melts with decomposition at 210° C., crystallises from water in brilliant scarlet plates which are soluble in cold alcohol, ether, chloroform, acetone, or boiling toluene, and are insoluble in light petroleum.

Thallium diethyl m-nitrophenoxide forms brownish-orange, oblong plates, M.pt. 196° C., after darkening at 194° C. The compound is less soluble in the above-named solvents than the ortho derivative.

Thallium diethyl p-nitrophenoxide crystallises from water in lemon-yellow, rhomboidal plates, darkening at 233° C. and melting at

[1] Goddard, *Trans. Chem. Soc.*, 1922, 121, 36.

238° C. It is less soluble in water than the ortho- and meta-compounds, only moderately soluble in alcohol, acetone, or chloroform, less soluble in ether, and insoluble in boiling toluene or light petroleum.

Thallium diethyl 2 : 4-dinitrophenoxide forms brownish-orange crystalline plates, M.pt. 174° C. The salt is easily soluble in hot pyridine, moderately soluble in alcohol, acetone, or ether, slightly soluble in chloroform or toluene, and insoluble in carbon tetrachloride or light petroleum.

Thallium diethyl 2 : 6-dinitrophenoxide forms deep orange plates, sintering at 182° C. and melting with decomposition at 190° C. The salt is completely soluble in cold alcohol, ether, or acetone, giving yellow solutions in pyridine, ethyl acetate, chloroform, or hot toluene, fairly soluble in carbon tetrachloride, and insoluble in light petroleum.[1]

Thallium diethyl 2 : 4 : 6-trinitrophenoxide crystallises from water in golden-yellow, oblong plates, which darken at 200° C. and melt with decomposition at 204° C. The salt is very soluble in water or cold alcohol, ether, chloroform, or acetone, moderately soluble in boiling toluene, and insoluble in light petroleum.

Thallium diethyl 4 : 6-dinitro-2-aminophenoxide gives small, carmine-red plates, which have a metallic lustre and explode violently when moistened with fuming nitric acid. The salt darkens at 140° C., melts with decomposition at 159° C., and is moderately soluble in alcohol, acetone, or pyridine, slightly soluble in chloroform, ether, or toluene, and insoluble in carbon tetrachloride or light petroleum.

Thallium diethyl hexanitrodiphenylamine crystallises in brilliant carmine plates, having a violet reflex, M.pt. 224° C. It is soluble in cold alcohol, acetone, ether, pyridine or ethyl acetate, and insoluble in toluene, light petroleum, chloroform, or carbon tetrachloride.

Thallium diethyl 4-nitrosophenoxide.—This salt is only isolated in the form of its acid salt, $C_{10}H_{14}O_2NTl.C_6H_4O_2N$. From water it is deposited in blue-black needles having a violet reflex, these crystals being completely soluble in pyridine, slightly soluble in acetone or alcohol, giving a brown solution in the latter, and insoluble in other organic solvents.

Thallium diethyl 3-nitro-o-tolyloxide crystallises in deep red plates having a green reflex, M.pt. 190° to 191° C., and is easily soluble in cold alcohol, ether, chloroform, pyridine, or boiling toluene, moderately soluble in water or hot carbon tetrachloride, and slightly soluble in light petroleum.

Thallium diethyl 4-nitro-m-tolyloxide gives pale red plates, darkening at 220° C. and exploding violently at 228° C. The salt is moderately soluble in alcohol, ether, or pyridine, slightly soluble in toluene, chloroform, or carbon tetrachloride, and insoluble in light petroleum.

Thallium diethyl 6-nitro-m-tolyloxide, obtained in small lemon-yellow plates, darkens at 210° C., and melts with decomposition at 216·5° C. It is easily soluble in cold pyridine, hot alcohol, or acetone, slightly soluble in ether or chloroform, and insoluble in carbon tetrachloride, toluene, or light petroleum.

Thallium diethyl 3-nitro-p-tolyloxide is deposited from aqueous solution in small, ruby-red, rhomboidal plates, having a green lustre. It softens at 200° C. and melts at 206° C., is easily soluble in hot

[1] Goddard, *Trans. Chem. Soc.*, 1923, 123, 1167.

pyridine, moderately soluble in chloroform or toluene, slightly soluble in alcohol, ether, acetone, or carbon tetrachloride, and insoluble in light petroleum.

Thallium diethyl 5-nitro-o-tolyloxide.—This derivative is obtained in the form of its acid salt, $C_{11}H_{16}O_9NTl.C_7H_7O_3N$, which softens at 165° C. and melts to a red liquid at 181·5° C. The salt crystallises in brownish-yellow plates, which are easily soluble in cold water, pyridine, warm alcohol, or acetone, moderately soluble in ether or chloroform, slightly soluble in toluene, and insoluble in carbon tetrachloride or light petroleum.

Thallium diethyl dinitro-o-tolyloxide crystallises in terra cotta plates, which blacken at 215° C. and explode with great violence at 219° C. It is completely soluble in cold pyridine or hot alcohol, ethyl acetate or acetone (giving yellow solutions in the two latter), moderately soluble in toluene, ether, or chloroform, and insoluble in carbon tetrachloride or light petroleum.

Thallium diethyl trinitro-m-tolyloxide forms brilliant, yellow needles, which sinter at 203° C. and decompose with gas evolution at 214° C. This compound has a similar solubility to the above dinitro derivative.

Thallium diethyl dinitro-β-naphthoxide crystallises in dull, greenish-yellow, microscopic, flat-ended blades which decompose at 208° C. The salt is completely soluble in pyridine or acetone, moderately soluble in alcohol, giving a reddish-yellow solution, slightly soluble in chloroform, ethyl acetate, or ether, becoming bright yellow in the latter, and insoluble in carbon tetrachloride, toluene, or light petroleum.

Thallium diethyl trinitro-α-naphthoxide is deposited in orange plates from aqueous solution, these sintering at 213° C. and melting with decomposition at 220° C. It is completely soluble in cold pyridine or acetone and hot ethyl acetate, moderately soluble in alcohol or ether, less so in chloroform or toluene, and insoluble in light petroleum or carbon tetrachloride.

Thallium diethyl α-nitroso-β-naphthoxide crystallises from alcoholic solution in deep green needles which melt with decomposition at 217° C. It is insoluble in light petroleum, and completely soluble in all other organic solvents, giving green solutions in alcohol or carbon tetrachloride, and brown solutions in other solvents.

Thallium diethyl 2 : 4 - dinitronaphthoxide - 7 - sulphonate is obtained in pale orange needles which darken at 217° C., but do not melt at 280° C. These crystals contain 2 mols. of water of crystallisation, and are completely soluble in cold acetone or warm pyridine, moderately soluble in alcohol, slightly in carbon tetrachloride, and insoluble in other organic solvents, the colour deepening in toluene.

Thallium dipropyl chloride is obtained by the action of magnesium n-propyl chloride on thallic chloride, the yield being 70 to 80 per cent. of the theory. The compound crystallises from dilute aqueous ammonia in glistening silver plates which decompose at 198° to 202° C. The *bromide* and *iodide* (M.pt. 183° to 185° C.) are isolated in the usual manner, and the *hydrosulphide* is more easily obtained than in the methyl and ethyl series.

Thallium dipropyl hydroxide is prepared as for the corresponding ethyl compound, but is only obtained as an oil, which does not solidify, and has not been analysed.

Thallium di-isopropyl chloride decomposes at 150° C., and its *nitrate* is sparingly soluble in water.

Thallium di-n-butyl fluoride [1] is obtained from the corresponding bromide by treatment with silver fluoride. It forms colourless needles, decomposing at 220° to 240° C. when rapidly heated. In alcohols or water it is readily soluble, sparingly in ether. When treated in aqueous solution with dilute hydrochloric acid, the *chloride* is obtained. This crystallises from pyridine in thick plates, from n-propyl alcohol in thin, colourless plates. It is sparingly soluble in water, and practically insoluble in ether. When rapidly heated to 240° or 250° C. it explodes. The *bromide* crystallises in plates from pyridine or alcohols, is sparingly soluble in water and explodes at 240° to 250° C. The *iodide* forms plates which explode on rapid heating, but when slowly heated decompose at 220° to 225° C., becoming first brown, then yellow. It is decomposed by nitric acid with the separation of iodine. The *sulphate* is obtained from the *carbonate*, the latter being formed by the action of sodium carbonate on the fluoride. The sulphate crystallises in plates or needles, M.pt. 156° to 158° C., when placed in a bath previously heated to 150° C. It explodes at 190° to 200° C. when rapidly heated. The *nitrate* forms thick plates from pyridine, and small needles from alcohols, which explode at 280° to 290° C.

Thallium di-isobutyl chloride crystallises from hot alcohol, pyridine, or benzene, as well as cold ether, in long, glistening, colourless needles. The corresponding *nitrate* is a difficultly soluble, crystalline precipitate.

Thallium di-isoamyl chloride explodes at 253° to 257° C., and the *fluoride* melts at 216° to 218° C. with decomposition. They have similar properties to the n-butyl compounds.

Thallium di-sec-butyl chloride explodes at about 150° C. and crystallises in colourless needles or plates, the form depending on the solvent used. The *nitrate* crystallises in plates.

Aryl Compounds of the Type R_2TlX.

Thallium diphenyl chloride.[2]—Sufficient dry ether is added to 5 grams of triphenylbismuthine to effect solution, followed by 3·54 grams of thallic chloride in the same solvent. A white precipitate is immediately thrown down, and this is extracted with acetone until free from diphenylchlorobismuthine. The product after boiling with glacial acetic acid is recrystallised several times from pyridine. It is thus obtained in colourless, microscopic needles, which do not melt at 300° C., and are slightly soluble in boiling glacial acetic acid, alcohol, ethyl acetate, or chloroform, and insoluble in ether, acetone, or light petroleum.

The same product may also be isolated by the interaction of mercury diphenyl (1 mol.) and thallic chloride (1 mol.) in dry ether. In this case, any mercury phenyl chloride which may be formed is removed by extraction with benzene, then further purification is carried out as above.

Thallium diphenyl bromide.[3]—10·3 grams of thallic chloride in

[1] Krause and Grosse, *Ber.*, 1925, 58, [B], 1933.
[2] Goddard, *Trans. Chem. Soc.*, 1922, 121, 256.
[3] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 257.

dry ether are slowly added to a solution of 23·8 grams of bromobenzene and 3·2 grams of magnesium ribbon in the same solvent. The mixture is cooled in ice during the operation, and after the reaction has subsided the whole is heated on the water-bath for half an hour, cooled, and decomposed with water. After filtering, the dried residue is extracted with pyridine, when transparent, microscopic needles are obtained which do not melt at 300° C. These are further purified as in the case of the chloride, and are insoluble in alcohol, chloroform, benzene, acetone, light petroleum, acetic acid, or ethyl acetate.

The *fluoride* melts at 305° to 310° C. with decomposition ; it is easily soluble in hot water, insoluble in ether.

Thallium di-o-tolyl chloride.—This compound is prepared by the action of thallic chloride on magnesium o-tolyl bromide, then boiling the product obtained with dilute hydrochloric acid. It crystallises from pyridine in slender, microscopic needles, which do not melt at 300° C. and are insoluble in all organic solvents.

Thallium di-p-tolyl chloride is isolated from the interaction of tri-p-tolylbismuthine and thallic chloride. It crystallises from pyridine in small, transparent needles, which remain unmelted at 300° C. and are slightly soluble in alcohol or acetone, and insoluble in chloroform, light petroleum, toluene, or alcoholic ammonia.

Thallium di-p-tolyl bromide is prepared as in the case of the corresponding phenyl compound. It forms pale yellow needles, which do not melt at 300° C. and are insoluble in all organic solvents with the exception of pyridine.

Thallium di-α-naphthyl chloride is a white, crystalline powder, unmelted at 300° C. and obtained from tri-α-naphthylbismuthine and thallic chloride. It is fairly soluble in hot pyridine, slightly soluble in glacial acetic acid, ethyl acetate, chloroform, or alcohol, and insoluble in ether, acetone, benzene, or carbon tetrachloride.

Thallium di-α-naphthyl bromide, prepared from magnesium α-naphthyl bromide and thallic chloride, is a fawn, crystalline powder, melting at 272° C. and is completely soluble in cold pyridine, insoluble in toluene.

Thallium di-cyclohexyl chloride [1] crystallises in long, colourless needles, exploding at 210° to 230° C., is soluble in warm alcohol or benzene, insoluble in hot water or warm ether.

Thallium diphenyl oxide.[2]—The chloride (4·5 grams) and 20 grams of potassium hydroxide, in a mixture of 30 c.c. of absolute alcohol and 20 c.c. of water, are heated under reflux for eight hours. The whole is then poured into water, the white flocculent mass thus obtained being washed free from potassium hydroxide. The oxide is a white, crystalline powder, unmelted at 300° C., and is completely soluble in pyridine, slightly soluble in alcohol, chloroform, or water, and insoluble in acetone, xylene, carbon tetrachloride, light petroleum, or ethyl acetate.

Thallium diphenyl nitrite [3] is obtained by boiling together thallium diphenyl bromide and silver nitrite in xylene solution for two and a half hours. The nitrite is deposited from pyridine in short, transparent needles, completely soluble in hot pyridine, slightly soluble in

[1] Krause and Grosse, *loc. cit.*
[2] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 486.
[3] Goddard and Goddard, *ibid.*, 487.

chloroform or alcohol, very slightly soluble in acetone, and insoluble in other organic solvents.

Thallium diphenyl nitrate has a similar crystalline form to the nitrite, is completely soluble in hot pyridine, very slightly soluble in boiling glacial acetic acid, water, or alcohol, and insoluble in other organic solvents.

Thallium diphenyl chromate crystallises from xylene in pale yellow, short needles which are completely soluble in pyridine and boiling glacial acetic acid, slightly soluble in acetone, and insoluble in water and other organic solvents.

Thallium diphenyl pyrophosphate crystallises from pyridine-ether solution in short, microscopic needles which are completely soluble in pyridine, moderately soluble in boiling glacial acetic acid, less soluble in alcohol, ethyl acetate, or chloroform, and insoluble in acetone, ether, carbon tetrachloride, or light petroleum.

Thallium diphenyl acetate is obtained by treating the oxide with boiling glacial acetic acid, the evaporated solution depositing fine, transparent needles, M.pt. 262° C. The salt is completely soluble in hot pyridine, chloroform, toluene, ethyl acetate, or alcohol, moderately soluble in carbon tetrachloride or water, slightly soluble in ether or acetone, and insoluble in light petroleum.

Thallium diphenyl acid propionate [1] forms fine silky needles from toluene, M.pt. 164° C., these being completely soluble in cold chloroform, hot alcohol, pyridine, ethyl acetate, or glacial acetic acid, fairly soluble in boiling water, and insoluble in ether or light petroleum.

Thallium diphenyl acid valerate.—M.pt. 176° C., forms fine white needles from toluene, having a similar solubility to the propionate.

Thallium diphenyl acid butyrate forms waxy needles, M.pt. 170° C., when dissolved in acetone the addition of light petroleum precipitates the *normal butyrate*, M.pt. 230° C.

Thallium diphenyl acid n-hexoate forms feathery rosettes of needles from toluene, M.pt. 191° C.; the *normal salt* obtained similarly to the butyrate melts at 208° C.

Thallium diphenyl n-octoate is deposited from toluene in waxy needles, M.pt. 195° C., and is less soluble than the acetate.

Thallium diphenyl p-nitrobenzoate forms faint yellow, blunt-ended needles, M.pt. 228° C., which are completely soluble in cold pyridine, hot acetone, toluene, or ethyl acetate, slightly soluble in alcohol or ether, and insoluble in light petroleum, chloroform, or carbon tetrachloride.

Thallium diphenyl o-bromobenzoate forms cream, glistening plates, M.pt. 243° C., to a clear liquid. The compound is fairly soluble in chloroform, insoluble in ether or light petroleum, and completely soluble in other organic solvents.

Thallium diphenyl m-bromobenzoate crystallises from toluene in glistening plates, M.pt. 247° C., the solubility of this salt being slightly less than the ortho compound.

Thallium diphenyl o-nitrophenoxide.—This is obtained by the interaction of thallium diphenyl oxide and o-nitrophenol, and is a bright orange, crystalline powder which turns scarlet on heating, reverting to its original colour on cooling. It melts to a blood-red liquid at 247° C., and is completely soluble in cold pyridine, fairly soluble in acetone or

[1] Goddard, *Trans. Chem. Soc.*, 1923, 123, 1164.

alcohol, giving yellow solutions, slightly soluble in toluene (becoming scarlet), ether, or hot water, insoluble in light petroleum, carbon tetrachloride, or ethyl acetate, being decolorised in the latter.

Thallium diphenyl p-nitrophenoxide.—When thallium diphenylchloride, silver oxide, and p-nitrophenol are boiled in xylene for three hours, and the product extracted with water, lemon-yellow needles of the above compound are obtained. It melts with decomposition at 250° C., and only differs slightly from the ortho compound in solubility.

Thallium diphenyl trinitro-m-tolyloxide forms yellow needles from water, melting with decomposition at 231° C. It is completely soluble in cold pyridine or acetone, and warm alcohol, ether, or ethyl acetate, fairly soluble in chloroform, slightly soluble in water, carbon tetrachloride, light petroleum, or toluene, becoming orange in the latter.

Thallium diphenyl α-nitroso-β-naphthoxide crystallises from ether in microscopic, green needles, melting with decomposition at 238° C. The salt gives green solutions in alcohol, acetone, pyridine, toluene, or carbon tetrachloride, and is brown in other solvents, but differs from the corresponding ethyl compound in its insolubility in water.

Thallium diphenyl trinitro-α-naphthoxide.—This salt crystallises in brilliant orange needles, which melt to a blood-red liquid at 232° C. With the exception of its complete solubility in hot alcohol, it resembles the corresponding ethyl derivative.

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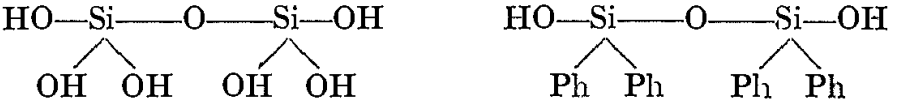
CHAPTER XII.

ORGANOMETALLIC DERIVATIVES OF THE METALS OF GROUP IV.

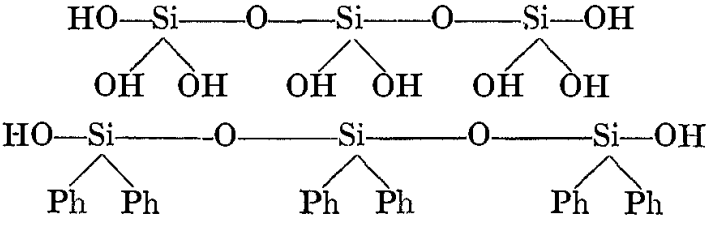
A CONSIDERABLE amount of work has been done during the past twenty years on the organic compounds of silicon, tin, and lead, and although the majority of the germanium derivatives are of recent date, this is probably due to the rarity and expense of this metal.

Silicon, being a non-metal, forms many types of compounds which could not be expected from the other three elements. Like carbon, it is capable of forming both chain and ring compounds, but with this essential difference, that whereas the carbon compounds consist of carbon to carbon linkages, the silicon usually links itself alternately with oxygen. Examples of such arrangements of atoms are shown as follows, together with any relationships which may exist with similar inorganic compounds :—

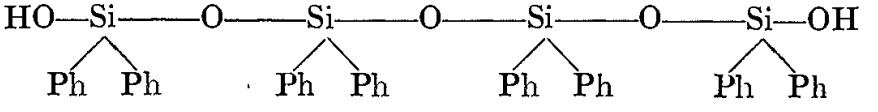
Orthodisilicic Acid Type, $H_6Si_2O_7$.



Orthotrisilicic Acid Type, $H_8Si_3O_{10}$.

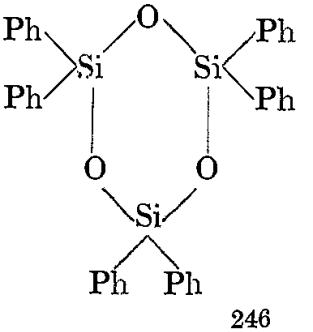


Orthotetrasilicic Acid Type, $H_{10}Si_4O_{13}$. (Free acid unknown.)

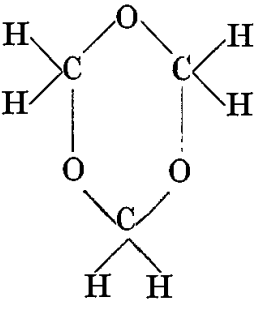


Germanium compounds corresponding to this tetrasilicic acid type are also known. Chain compounds which have corresponding cyclic anhydrides, formed by condensation and elimination of water, are given below :

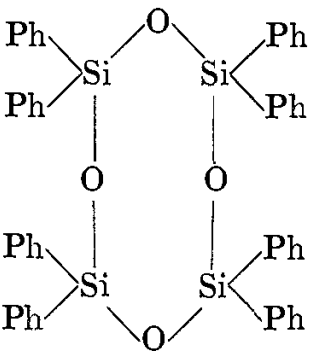
$(HO)_2SiPh_2$



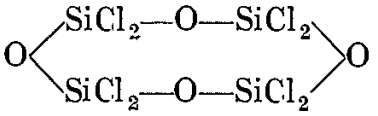
compare

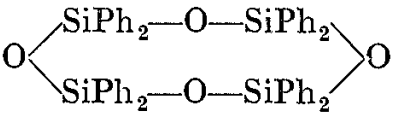


$HO.SiPh_2.O.SiPh_2.OH$



Caven [1] has also pointed out that the oxychloride, $Si_4O_4Cl_8$, may have a cyclic constitution, which has an organic analogue,





Silicon also resembles carbon in forming ketones of the type R.SiO.R, but the likeness between the two classes ends with the formulæ. The following comparison has been drawn between the hydrocarbons and the silicon hydrocarbons :—[2]

Hydrocarbon.	Boiling-point. (760 mm.).	Silicon Hydrocarbon.	Boiling-point. (760 mm.).
$Me_3C.CMe_3$	106·0° C.	$Me_3Si.SiMe_3$	113·0° C.
$Me_3C.Ph$	168·2° C.	$Me_3Si.Ph$	171·6° C.
$Me_2C.EtPh$	189·0° C.	$Me_2Si.EtPh$	198·0° C.
$Et_3C.Ph$	221·0° C.	$Et_3Si.Ph$	238·3° C.

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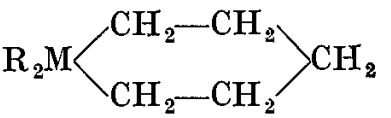
The gradation in melting-points and boiling-points in passing from silicon to lead, for some derivatives of the elements of Group IV., is shown in Table V. of the Appendix.

Tin and lead differ from silicon in forming divalent and tervalent compounds, and tin also forms hydrides of the type SnR_3H and SnR_2H_2. The tervalent compounds show true tervalency in dilute solution only, for if the molecular weights by the freezing-point methods are carried out with increasing concentration of solute, association appears to take place.

The only ring compounds formed by tin and lead are of the type



and those derivatives containing two atoms of the same metal are shown by

$$R_3M.MR_3\ ;\quad R_3M(CH_2)_5MR_3\ ;\quad R_3Sn(CH_2)_{10}SnR_3$$

Cases are also known in this group in which two different metals are present in the same compound :

$$Me_3Sn(CH_2)_5PbMe_3\ ;\quad Et_3Si.C_6H_4.PbMe_3\ ;\quad Et_3Si.C_6H_4.SnEt_3\ ;\quad Et_3Si.C_6H_4.AsPh_2$$

[1] Caven, this series, Vol. v. (1917), p. 203.
[2] Bygdén, *Ber.*, 1912, 45, 707.

Silicon.

Most of the work carried out on this element is due to Kipping and his co-workers, and the investigations are a model of patience and perseverance. Although many of the substances formed appear as glue-like products, an enormous mass of information regarding the organic compounds of this element has been collected together. The following system of nomenclature for organic silicon derivatives is due to Kipping:—[1]

The term *silicane*, used for silicon hydride, is maintained for analogous derivatives of CH_4. The radicle SiH_3 is termed *silicyl*, and corresponds to CH_3, *e.g.* $SiPh_3Cl$, triphenylsilicyl chloride. *Silicanol* and *silicanediol* are used for hydroxy derivatives:

$SiH_3.OH$	$SiPh_3OH$	$SiH_2(OH)_2$	$SiPh_2(OH)_2$
Silicanol.	Triphenylsilicanol.	Silicanediol.	Diphenylsilicanediol.

The term *silicone* denotes analogues of ketones, *e.g.* $SiEt_2O$, diethylsilicone. Owing to the dissimilarity between the ethers and the corresponding silicon compounds containing $\begin{matrix}Si\\ \\ Si\end{matrix}\!\!>\!O$, the term oxide is employed, thus:

$$\begin{matrix}SiPh_3\\ \\ SiPh_3\end{matrix}\!\!>\!O$$

is known as triphenylsilicyloxide.

The following names show how many molecules of silicanediol have condensed together, and how many molecules of water are eliminated in the process:—

$SiPh_2OH$

$|^1$

O

$|$

$SiPh_2OH$

Anhydrobisdiphenylsilicanediol.

$SiPh_2OH$

$|$

O

$|$

$SiPh_2$

$|$

O

$|$

$SiPh_2OH$

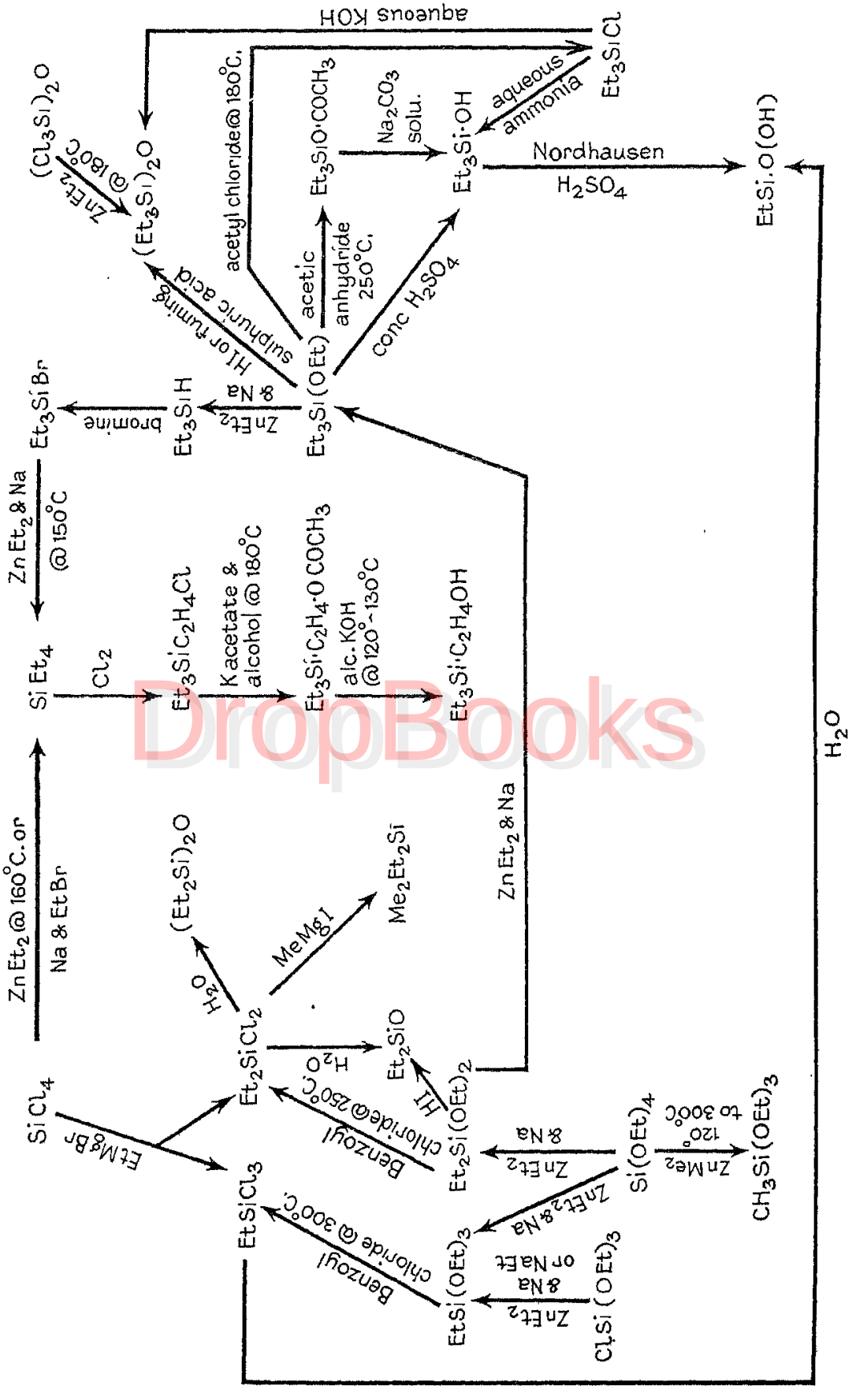
Dianhydrotrisdiphenylsilicanediol.

In order to show how it is possible to pass from one type of aliphatic compound to another, the scheme shown on opposite page has been drawn up, using the ethyl derivatives as examples.

Alkyl Derivatives of the Type R_4Si.

Tetramethylsilicane, $Si(CH_3)_4$.—This compound is obtained by heating together zinc dimethyl and silicon tetrachloride in a sealed

[1] Kipping, *Trans. Chem. Soc.*, 1912, 101, 2106.


aqueous KOH
$(Cl_3Si)_2O$
$Zn Et_2$ @ 180°C
$(Et_3Si)_2O$
Et_3SiCl
aqueous ammonia
$Et_3Si{\cdot}OH$
Nordhausen H_2SO_4
$EtSi{\cdot}O(OH)$
Na_2CO_3 solu.
$Et_3Si{\cdot}OCOCH_3$
acetyl chloride @ 180°C.
acetic anhydride 250°C.
conc H_2SO_4
HI or fuming sulphuric acid
$Et_3Si(OEt)$
Et_3SiH
Zn Et_2 & Na
Et_3SiBr
bromine
$Zn Et_2$ & Na @ 150°C
$Si Et_4$
Cl_2
$Et_3Si{\cdot}C_2H_4Cl$
K acetate & alcohol @ 180°C
$Et_3Si{\cdot}C_2H_4{\cdot}O\,COCH_3$
alc. KOH @ 120°-130°C
$Et_3Si{\cdot}C_2H_4OH$
H_2O
$Zn Et_2$ @ 160°C. or Na & EtBr
$Si Cl_4$
Et_2SiCl_2
H_2O
$(Et_2Si)_2O$
MeMgI
Me_2Et_2Si
H_2O, 250°C
Et_2SiO
$Zn Et_2$ & Na
$Et_2Si(OEt)_2$
HI
Benzoyl chloride @ 250°C
EtMgBr
$EtSiCl_3$
$Zn Et_2$ & Na
$Si(OEt)_4$
$Zn Me_2$ 120° to 300°C
$CH_3Si(OEt)_3$
$Zn Et_2$ & Na
$EtSi(OEt)_3$
Benzoyl chloride @ 300°C.
$Zn Et_2$ & Na or Na Et
$ClSi(OEt)_3$

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tube at 200° C.[1] It boils at 30° to 31° C. and is a clear liquid, lighter than water. When treated with excess of methyl alcohol at 250° C. for fifteen hours, the *methyl ether* is obtained as a colourless liquid, B.pt. 121° to 126° C.; density 1·0589. In 1911 Bygdén[2] prepared tetramethylsilicane, using silicon tetrachloride and magnesium methyl bromide, and found its boiling-point to be 26° to 27° C.

Tetraethylsilicane[3] may be prepared by heating silicon tetrachloride and zinc diethyl at 160° for three hours;[4] or by the interaction of silicon triethyl ethyl ether, zinc ethyl, and sodium, these yielding the hydride $SiH.(C_2H_5)_3$. This with bromine forms triethyl silicon bromide, and further action of zinc ethyl and sodium at 150° C. produce tetraethylsilicane. It may also be prepared by the Wurtz reaction,[5] using silicon tetrachloride, sodium, and ethyl bromide. Tetraethylsilicane is a liquid, lighter than water, and it burns with a luminous flame, leaving a deposit of silica. Its boiling-point is variously given as 152° to 154° C.,[6] and 151° to 153° C.[7] With chlorine it gives triethylchlorethylsilicane, $(C_2H_5)_3Si.C_2H_4Cl$.

Tetrapropylsilicane[8] is obtained along with tripropylsilicane by the action of zinc propyl on silicochloroform (trichlorosilicane) at 120° to 150° C. The lower fraction is tripropylsilicane and the higher one tetrapropylsilicane. The reaction is probably represented thus:

$$2SiHCl_3+4Zn(C_3H_7)_2=SiH(C_3H_7)_3+Si(C_3H_7)_4+3ZnCl_2+Zn+C_3H_8$$

The silicane may also be produced by the interaction of silicon tetrachloride, propyl iodide, and zinc at 180° C.:

$$SiCl_4+4C_3H_7I+4Zn=Si(C_3H_7)_4+2ZnCl_2+2ZnI_2$$

Tetrapropylsilicane is a colourless, almost odourless oil, which burns with a sooty flame, depositing silica; it is soluble in alcohol or ether, and insoluble in water or concentrated sulphuric acid. It boils at 213° C.; density 0·7979 at 0° C., 0·7883 at 15° C. It is not attacked by concentrated sulphuric or nitric acids or by potassium hydroxide, but bromine on warming readily substitutes. The compound can be purified by the use of concentrated sulphuric acid, as was done in the case of tetraethylsilicane.[9] Removal of tripropylsilicane and oxide is thus effected.

Tetra-isoamylsilicane[10] is obtained from silicon tetrachloride, sodium, and isoamyl chloride. An oily residue remains after distilling off the tetra-isoamylsilicane. It is colourless, feebly fluorescent, boiling between 360° and 370° C., and is found to be silicon tri-isoamyloxide. Tetra-isoamylsilicane is a colourless, odourless liquid, B.pt. 275° to 279° C., and miscible with alcohol and ether in all proportions.

[1] Friedel and Crafts, *Annalen*, 1865, 136, 203.
[2] Bygdén, *Ber.*, 1911, 44, 2640.
[3] Friedel and Crafts, *Annalen*, 1863, 127, 28.
[4] Ladenburg, *Annalen*, 1872, 164, 300.
[5] Kipping and Lloyd, *Trans. Chem. Soc.*, 1907, 79, 209.
[6] Friedel and Crafts, *loc. cit.*
[7] Ladenburg, *loc. cit.*
[8] Pape, *Annalen*, 1884, 222, 354.
[9] Friedel and Crafts, *Ann. Chim. Phys.*, 1895, [4], 19.
[10] Taurke, *Ber.*, 1905, 38, 1661.

Alkyl Derivatives of the Type R_3SiR'.

Triethylsilicane, $(C_2H_5)_3SiH$.[1]—This is formed by the interaction of zinc ethyl, sodium, and silicoheptyl ethyl ether. It is a colourless liquid, boiling at 107° C., and of density 0·7510 at 0° C. It is soluble in both alcohol and ether, but insoluble in water and in concentrated sulphuric acid. With fuming sulphuric acid it reacts according to the equation :

$$2SiEt_3H + 2SO_3 = (Et_3Si)_2O + H_2O + 2SO_2$$

With bromine it forms triethyl silicon bromide.

Tripropylsilicane [2] is produced by heating one part of silicochloroform (trichlorosilicane) and two parts of zinc propyl in a sealed tube at 150° C. for six hours :

$$2SiHCl_3 + 3ZnPr_2 = 2SiHPr_3 + 3ZnCl_2$$

The product obtained is a colourless oil. This is washed with water, then dried over calcium chloride and fractionated. Tripropylsilicane distils between 170° and 175° C. ; the residue is tetrapropylsilicane. Tripropylsilicane is a colourless, pungent, fuming liquid, and burns with a luminous, sooty flame. It boils at 170° to 171° C., density 0·7723 at 4° C., 0·7621 at 15° C., and is difficult to free from the tetrapropyl body. To prevent decomposition it should be distilled in a stream of hydrogen. The compound is easily soluble in alcohol or ether, but insoluble in water or concentrated sulphuric acid. With the latter, however, feeble oxidation occurs in the cold, with evolution of sulphur dioxide, and on warming tripropylsilicon oxide is formed.

Tri-isobutylsilicane may be prepared [3] by interaction of trichlorosilicane, isobutyl chloride, and sodium. It is a colourless, odourless liquid, B.pt. 204° to 206° C.

Tri-isoamylsilicane has been prepared in the same way as the above, using isoamyl chloride. It is a feebly fuming liquid, B.pt. 245° C., soluble in alcohol or ether, and unattacked by water or potassium hydroxide.

Trimethylethylsilicane [4] is obtained by the action of methyl magnesium bromide on trichloroethysilicane. The product is extracted with ether, washed with concentrated sulphuric acid, and on distillation boils between 62° and 70° C., the main portion distilling at 62·5° to 63·5° C.

Trimethyl-n-propylsilicane is prepared similarly to the above, using propyltrichlorosilicane.

Trimethyl-n-butylsilicane.—It is first necessary to obtain n-butyltrichlorosilicane by the action of n-butyl magnesium bromide on silicon tetrachloride. The product, boiling at 147° to 151° C., is a liquid, fuming in moist air, and when treated with methyl magnesium bromide, trimethyl-n-butylsilicane is formed, B.pt. 115° C.

Trimethyl-isobutylsilicane is difficult to obtain, because the isobutyltrichlorosilicane is troublesome to prepare. The methyl Grignard reagent gives trimethyl-isobutylsilicane, B.pt. 107·9° to 108·2° C.

[1] Ladenburg, *Annalen*, 1872, 164, 300
[2] Pape, *Annalen*, 1884, 222, 354.
[3] Taurke, *Ber.*, 1905, 38, 1661.
[4] Bygdén, *Ber.*, 1911, 44, 2640.

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Trimethyl-isoamylsilicane is prepared as the above two compounds, the starting-point being isoamyltrichlorosilicane.[1] The body boils at 131° to 132° C.

Triethylchloroethylsilicane, $(C_2H_5)_3SiC_2H_4Cl$, may be obtained by[2] passing chlorine into tetraethylsilicane in water; hydrogen chloride is evolved, and a yellow oil separates. Two fractionations yield a liquid, B.pt. 185° C., in small quantity, which is triethylchloroethylsilicane.

Triethylacetoxyethylsilicane, $(C_2H_5)_3SiC_2H_4.O.CO.CH_3$. — The fraction, B.pt. 180° to 190° C., of the above triethylchloroethylsilicane when heated in a sealed tube with potassium acetate and alcohol for several hours at 180° C. yields a liquid, B.pt. 208° to 214° C. It has a faint ethereal and acetic acid odour, burns with a luminous flame, and is found to be the acetate.

Triethylhydroxyethylsilicane is produced from the above when it is treated with dilute alcoholic potassium hydroxide at 120° to 130° C., and has been proved to be a liquid of the composition $(C_2H_5)_3SiC_2H_4OH$. It boils at about 190° C. and is insoluble in water.

Triethyl-n-propylsilicane[3] is prepared in a similar manner to the corresponding trimethylsilicanes, using n-propyltrichlorosilicane[4] and ethyl magnesium bromide. The compound boils between 172·8° and 173·2° C. It is partly soluble in concentrated sulphuric acid, giving a product, B.pt. 160° to 225° C., and is therefore not homogeneous.

Triethyl-n-butylsilicane is prepared[5] in the same manner as the above compound. It boils at 190·6° to 191·6° C.

Triethyl-isobutylsilicane, prepared as above, boils at 187° to 187·2° C., and **triethyl-isoamylsilicane** boils at 204·6° to 205·6° C.

Alkyl Derivatives of the Type R_2SiR_2'.

Dimethyldiethylsilicane[6] is obtained from diethyl silicon chloride (24·5 grams), using 2 mols. of methyl magnesium iodide. The chief fraction, B.pt. 95° to 96° C., weighs 6 grams.

Dimethyldipropylsilicane is prepared in the same manner as the above. It boils at 140° to 142° C.

Alkyl Derivatives of the Type $R_2SiR'R''$.

Dimethylethyl-n-propyl-silicane.—It is first necessary to obtain ethyl-n-propylsilicon chloride, which may be formed by one of two methods. (1) From ethyltrichlorosilicane by replacing one chlorine with the propyl group. (2) From propyltrichlorosilicane by removing one chlorine and putting in an ethyl group. The latter method is utilised and the ethyl introduced by ethyl magnesium bromide, when five fractions are isolated. The one, B.pt. 152° to 154° C., gives the best analysis. This fuming liquid, $Et.Pr.SiCl_2$, with methyl magnesium bromide gives the desired compound, B.pt. 120° to 122° C.

Dimethylethyl-isobutylsilicane is prepared in a similar manner to

[1] Melser, *Ber.*, 1908, 41, 3392.
[2] Friedel and Crafts, *Annalen*, 1866, 138, 19.
[3] Bygdén, *Ber.*, 1912, 45, 707.
[4] Melser, *Ber.*, 1908, 41, 3390.
[5] Bygdén, *loc. cit.*
[6] Bygdén, *Ber.*, 1911, 44, 2640.

the above, using isobutyltrichlorosilicane and ethyl magnesium bromide. The ethyl-isobutyl silicon chloride thus formed, with methyl magnesium bromide gives a product, B.pt. 137° to 139° C.

Alkyl Derivatives of the Type R_3SiX.

Triethylchlorosilicane, $(C_2H_5)_3SiCl$, is obtained [1] by the interaction of silicon triethyl ethyl ether and acetyl chloride, thus:

$$(C_2H_5)_3SiOC_2H_5+CH_3COCl=(C_2H_5)_3SiCl+CH_3CO.OC_2H_5$$

This reaction requires a sealed tube and a temperature of 180° C. Triethylchlorosilicane boils at 143° to 145° C., has density at 0° C. 0·9249, is only slowly decomposed by water, and with silver nitrate precipitates silver chloride. Triethyl silicol is formed by the action of ammonia, and triethyl silicon oxide is produced with water.

Triethylbromosilicane is formed by the action of bromine on triethylsilicane. It boils at 161° C., is slowly decomposed by water, and the bromine is easily replaced by hydroxyl by aqueous potassium hydroxide or sodium carbonate. By treatment with zinc ethyl and sodium at 150° C. tetraethylsilicane is produced.

Triethyl silicon acetate is formed when acetic anhydride is allowed to react with silicon triethyl ethyl ether in a sealed tube at 250° C.:

$$(C_2H_5)_3SiOC_2H_5+(CH_3CO)_2O=(C_2H_5)_3SiO.CO.CH_3+CH_3.CO.OC_2H_5$$

Tripropylbromosilicane.[2] — When 1 mol. of tripropylsilicane is treated with 1 mol. of bromine and cooled, hydrobromic acid is evolved. The reaction is allowed to finish on the water-bath and goes smoothly, giving a good yield. On fractionation the product obtained is a yellow, fuming oil, B.pt. 213° C., which decomposes slowly in the air, evolving hydrobromic acid. With water it slowly changes, while aqueous ammonia completely converts it to tripropyl silicol, B.pt. 205° to 208° C., and a little tripropylsilicon oxide.

Tripropyl silicon acetate is obtained from the bromide by the action of dry silver acetate, cooling being necessary from time to time:

$$Pr_3SiBr+AgC_2H_3O_2=Pr_3Si.C_2H_3O_2+AgBr$$

The body is a colourless oil, B.pt. 212° to 216° C., slowly changing in air to tripropylsilicol and acetic acid.

Tri-isobutylbromosilicane [3] is prepared by the bromination of tri-isobutylsilicane. It is a yellow, fuming liquid, heavier than water, B.pt. 245° C.

Tri-isoamylbromosilicane, obtained in the above manner, boils at 278° to 280° C., and has similar properties to the preceding body.

Alkyl Derivatives of the Type R_2SiX_2.

Diethyl silicon dichloride was prepared by Ladenburg [4] by treating silicon diethyl ether with benzoyl chloride at 250° C. The body is identical with that obtained by the action of hydrogen iodide on silicon

[1] Ladenburg, *Annalen*, 1872, 164, 300.
[2] Pape, *Annalen*, 1884, 222, 354.
[3] Taurke, *Ber.*, 1905, 38, 1661.
[4] Ladenburg, *loc. cit.*

diethyl ether, or by using ethyl magnesium bromide and silicon tetrachloride.[1] The separation of the compound is, however, difficult, owing to formation of the three chloro-derivatives, whose boiling-points lie very close together. Diethyl silicon chloride is a colourless liquid, fuming in air and boiling at 128° to 130° C. With water it yields *diethyl silicone*, $(C_2H_5)_2SiO$, which is a syrupy body, easily soluble in ether, but difficultly soluble in alcohol. This silicone polymerises, giving a compound of high molecular weight.

Dibromoethyl silicon dichloride, $(CH_2Br.CH_2)_2SiCl_2$, is produced by heating together a mixture of two molecular proportions of ethylene bromide with 1 mol. of silicon tetrachloride dissolved in ether, and four molecular proportions of sodium and a little ethyl acetate. The product is a dark brown oil.[2] Doubt has recently been expressed as to the existence of this compound.[3]

Alkyl Derivatives of the Type $RSiX_3$.

Ethyl silicon trichloride, $C_2H_5SiCl_3$, is prepared from silicon ethyl triethyl ester and benzoyl chloride by heating them in a sealed tube at 300° C.[4]

$$SiEt(OEt)_3 + 3PhCOCl = EtSiCl_3 + 3PhCOOEt.$$

The liquid, B.pt. about 100° C., fumes considerably in moist air, and with water gives silicopropionic acid and hydrogen chloride. The trichloride has also been obtained from silicon tetrachloride. using the ethyl Grignard reagent.[5] It is a pale yellow, fuming liquid, B.pt. 97° to 103° C.

Propyl silicon trichloride[6] is formed by the action of propyl magnesium bromide on silicon tetrachloride, and is a clear, colourless liquid, B.pt. 123° to 125° C. In preparing the chloride all traces of moisture must be absent. It has a penetrating odour and fumes in the air. By allowing the liquid to drop into ice-water, the acid, PrSiO.OH, is obtained, and with anhydrous alcohol the trichloride gives silicon propyl triethyl ester, $PrSi(OEt)_3$.

Isoamyl silicon trichloride is produced in a similar manner to the above, and is a colourless, transparent, fuming liquid with a penetrating odour. It boils at 46° C. at 9 mm., and has a density of 1·066. Its reactions are the same as the propyl compound.

Alkyl Derivative of the Types $R_3Si(OH)$ *and* $R_3Si(OR)$.

Triethylsilicol, $(C_2H_5)_3Si.OH$, is isolated[7] by treating triethyl silicon acetate with sodium carbonate solution:

$$2(C_2H_5)_3SiO.CO.CH_3 + Na_2CO_3 + H_2O = 2(C_2H_5)_3Si.OH + 2NaO.CO.CH_3 + CO_2$$

[1] Martin and Kipping, *Trans. Chem. Soc.*, 1909, 95, 302.
[2] Hart, *Jahresber.*, 1889, p. 1943.
[3] Widdowson, *J. Chem. Soc.*, 1926, p. 958.
[4] Ladenburg, *Annalen*, 1872, 164, 300.
[5] Kipping, *Trans. Chem. Soc.*, 1907, 91, 209.
[6] Melzer, *Ber.*, 1908, 41, 3390.
[7] Ladenburg, *loc. cit.*

It may also be prepared by the action of aqueous ammonia on triethyl silicon chloride:

$$(C_2H_5)_3SiCl + NH_3 + H_2O = (C_2H_5)_3Si.OH + NH_4Cl$$

Another method of preparation consists in heating silicon triethyl ethyl ether with concentrated sulphuric acid and precipitating the product with water. The silicol is a colourless liquid with a strong camphor-like odour, B.pt. 184° C., density 0·8709 at 0° C., insoluble in water, but miscible with ether or alcohol. It burns with a dazzling flame, leaving a deposit of silica. If heated with sodium, hydrogen is evolved, and when carbon dioxide is passed into the ethereal solution and the solvent then evaporated, the sodium salt of triethyl silicon carboxylic acid, $(C_2H_5)_3SiCOONa$, is left. The following represent further reactions of triethyl silicol:—

$$(C_2H_5)_3SiOH + SO_3 = C_2H_5SiO.OH + 2C_2H_4 + H_2 + SO_2$$

(Nordhausen sulphuric acid.)

$$(C_2H_5)_3Si.OH \xrightarrow[\text{At } 200^\circ \text{ C.}]{HI,\ \text{B.pt. } 127^\circ \text{ C.}} (C_2H_5)_2SiO + C_2H_6$$

$$2(C_2H_5)_3Si.OH \xrightarrow{P_2O_5} [(C_2H_5)_3Si]_2O + H_2O$$

Silicon triethyl ethyl ether or **Silicoheptyl ethyl ether**, $(C_2H_5)_3Si(OC_2H_5)$, is obtained [1] by the interaction of zinc ethyl, sodium, and silicon diethyl diethyl ether, $(C_2H_5)_2Si(O.C_2H_5)_2$. It is a colourless liquid, B.pt. 153° C., density 0·8414, 0·8393, 0·8403 at 0° C., insoluble in water, miscible with alcohol or ether, and stable in air. Acetyl chloride acting on the compound gives rise to triethyl silicon chloride.

Tripropylsilicol, $(CH_3CH_2CH_2)_3SiOH$,[2] may be prepared in two ways:

1. From tripropyl silicon acetate by long boiling with 30 per cent. sodium carbonate only gives a small yield, a contrast to the formation of triethylsilicol. The poor yield is probably owing to the following reaction taking place:—

$$2Si(C_3H_7)_3O.CO.CH_3 + Na_2CO_3 = Si_2O(C_3H_7)_6 + 2NaO.CO.CH_3 + CO_2$$

2. When tripropyl silicon bromide is treated with aqueous ammonia the following two reactions occur simultaneously, so that the yield is little better:—

$$(C_3H_7)_3SiBr + NH_3 + H_2O = Si(C_3H_7)_3OH + NH_4Br$$
$$2(C_3H_7)_3SiBr + 2NH_3 + H_2O = Si_2O(C_3H_7)_6 + 2NH_4Br$$

Tripropyl silicol is a colourless, fuming oil, and is glycerine-like in consistency. It is lighter than water and insoluble in it. It dissolves in alcohol or ether and has a boiling-point of 206° to 208° C. When warmed with sodium, hydrogen is easily evolved and an amorphous mass remains, which is no doubt the *alcoholate*, since on warming with water the silicol is regenerated together with sodium hydroxide.

[1] Ladenburg, *loc. cit.*
[2] Pape, *Annalen*, 1884, 222, 354.

Tri-isoamylsilicol, $(C_5H_{11})_3SiOH$,[1] is formed by the action of aqueous ammonia on tri-isoamyl silicon bromide:

$$(C_5H_{11})_3SiBr + NH_4OH = (C_5H_{11})_3SiOH + NH_4Br$$

It boils at 269° to 270° C., has a penetrating smell, and is lighter than water. Metallic sodium dissolves in it with hydrogen evolution, probably forming the sodium derivative $(C_5H_{11})_3SiONa$.

Alkyl Derivatives of the Types $R_2Si(OR)_2$ *and* $R_2Si(OR).Hal.$

Silicon diethyl diethyl ether, $(C_2H_5)_2Si(OC_2H_5)_2$, is obtained by allowing silicon tetraethyl ester, $Si(OC_2H_5)_4$, to interact with sodium and zinc ethyl.[2] The ether produced is a colourless, fuming liquid, B.pt. 155·8° C.; density at 0° C. 0·8752. It is stable in air, insoluble in water, soluble in ether or alcohol, and unattacked by ammonia.

Diethylchlorosilicon ethyl ether, $(C_2H_5)_2Si(OC_2H_5)Cl$, is prepared from the above by the action of acetyl chloride. It boils at 146° to 148° C. and burns with a green flame, leaving a residue of silica.

Alkyl Derivatives of the Type $RSi.(OR)_3$.

Methyl triethoxy silicon or **Orthosilicoacetic acid triethyl ester**, $CH_3Si(OC_2H_5)_3$,[3] is formed by the interaction of tetraethoxysilicon, $Si(OC_2H_5)_4$, 15 grams, and 10 grams of zinc methyl at 120° C., then 300° C. The tubes are opened occasionally to allow escape of gases. It is a liquid, B.pt. 146° to 151° C., density at 0° C. 0·9283, and is insoluble in water. With ammonia or heating with hydrogen iodide, methyl monosilicic acid, $CH_3SiO.OH$, is formed.

Ethyl trimethoxy silicon, $C_2H_5Si(OCH_3)_3$, is prepared from tetramethoxysilicon, zinc ethyl, and sodium. It is a liquid, B.pt. 125° to 126° C., density at 0° C. 0·9747.

Ethyl triethoxy silicon, $C_2H_5Si(OC_2H)_3$, is isolated in the above manner from tetraethoxysilicon.[4] Another method of preparation is from triethoxysilicon chloride, using sodium and zinc ethyl. The reaction mixture gives a colourless liquid with a camphor-like odour, B.pt. 158·5° C., density at 0° C. 0·9207; it is insoluble in water, but miscible with alcohol and ether. It is not completely decomposed by alcoholic potassium hydroxide or ammonium hydroxide, but is broken up by concentrated sulphuric acid.[5]

Propyl triethoxy silicon or **Ethyl orthosilico-butyrate**, $C_3H_7Si(OC_2H_5)_3$,[6] is formed from propylsilicon trichloride by the use of absolute alcohol, and is a colourless liquid with an aromatic odour, B.pt. 177° to 179° C., density at 0° C. 0·8945.

Isoamyl triethoxy silicon is produced in the same manner as the above compound from isoamylsilicon trichloride. The liquid is pleasant smelling and boils at 195° to 200° C., density at 0° C. 0·9318.

[1] Taurke, *Ber.*, 1905, 38, 1661.
[2] Ladenburg, *Annalen*, 1872, 164, 300.
[3] Ladenburg, *Annalen*, 1874, 173, 148; *Ber.*, 1873, 6, 1029.
[4] Ladenburg, *Annalen*, 1872, 164, 300.
[5] Friedel and Ladenburg, *Annalen*, 1871, 159, 259.
[6] Melzer, *Ber.*, 1908, 41, 3391.

Alkyl Derivative of the Type $Si(OR)_3Hal$.

Chlorotriethoxysilicon, $SiCl(OC_2H_5)_3$.[1]—This is prepared according to the following equations:—

1. $Si(OC_2H_5)_4+CH_3COCl=SiCl(OC_2H_5)_3+CH_3COOC_2H_5$
2. $SiCl_4+3Si(OC_2H_5)_4=4SiCl(OC_2H_5)_3$
3. $SiCl_4+3C_2H_5OH=SiCl(OC_2H_5)_3+3HCl$

The last reaction requires absolute alcohol, and a sealed tube at 160° C. for several hours.

The compound is a liquid, B.pt. 156° C. With sodium ethyl it forms ethyltriethoxysilicon:

$$SiCl(OC_2H_5)_3+NaC_2H_5=NaCl+C_2H_5Si(OC_2H_5)_3$$

Alkyl Derivatives of the Type $(R_3Si)_2O$.

Triethyl silicon oxide or **Bis-(triethylmonosilyl)-ether,** $[(C_2H_5)_3Si]_2O$, may be prepared by several methods,[2] and the reactions are represented by the following equations:—

1. $2(C_2H_5)_3Si(OC_2H_5)+2HI=(C_2H_5)_3Si-O-Si(C_2H_5)_3+2C_2H_5I+H_2O$
2. $2(C_2H_5)_3Si(OH) \xrightarrow{P_2O_5} [(C_2H_5)_3Si]_2O+H_2O$
3. $2(C_2H_5)_3SiOC_2H_5+H_2SO_4 \underset{\text{(fuming)}}{=} [(C_2H_5)_3Si]_2O+2C_2H_5HSO_4+H_2O$
4. $2(C_2H_5)_3SiCl+2KOH \underset{\text{(aqueous)}}{=} [(C_2H_5)_3Si]_2O+2KCl+H_2O$

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It is also obtained from bis-(trichloromonosilyl)-ether, $Cl_3Si-O-SiCl_3$, by the action of zinc ethyl:[3]

$$Si_2Cl_6O+3Zn(C_2H_5)_2=[(C_2H_5)_3Si]_2O+3ZnCl_2$$

One molecule of silicon oxychloride is treated with the theoretical quantity (3 mols.) of zinc ethyl in a sealed tube at 180° C. for a prolonged period. The zinc ethyl disappears, and after treating the product with concentrated sulphuric acid an oil is obtained, which after washing and drying gives a main fraction distilling between 230° and 235° C. This is purified by several further fractionations and gives an analysis for triethyl silicon oxide. The compound is a colourless syrup, B.pt. 231° C., density at 0° C. 0·8590. It is soluble in concentrated sulphuric acid, and may be precipitated unchanged by the addition of water.

Tripropyl silicon oxide or Bis-(tripropylmonosilyl)-ether, $[(C_3H_7)_3Si]_2O$, is prepared from tripropylsilicane by the action of fuming sulphuric acid. The product is poured into well cooled water, when a yellowish oil separates, which is taken up with ether and dried over calcium chloride.[4] The oxide is also produced as a by-product from

[1] Friedel and Ladenburg, *Ber.*, 1870, 3, 15; *Annalen*, 1871, 159, 259.
[2] Ladenburg, *Annalen*, 1872, 164, 300.
[3] Friedel and Ladenburg, *Annalen*, 1868, 147, 355.
[4] Pape, *Annalen*, 1884, 222, 354.

tripropylsilicon bromide, when preparing the silicol with ammonia. It is formed along with the silicol when tripropyl silicon acetate is acted on with aqueous sodium hydroxide. The oxide is a yellow, almost odourless oil, soluble in alcohol or ether, and boils between 280° and 290° C.

Tri-isoamyl silicon oxide, $[(C_5H_{11})_3Si]_2O$, is produced [1] in the preparation of tetra-isoamylsilicane from silicon tetrachloride, sodium, and isoamyl chloride. It is contained in the oily residue which distils at 360° to 370° C. It has a glycerine-like consistency and is feebly fluorescent.

Alkyl Derivatives of the Type R_2SiO.

Diethylsilicone or **Diethylsilicon oxide,** $(C_2H_5)_2SiO$, is formed from silicon diethyl diethyl ether, which must first be converted into the dichloride, for which purpose benzoyl chloride is used at 250° C. With water the silicone is formed:

$$(C_2H_5)_2SiCl_2+H_2O=(C_2H_5)_2SiO+2HCl$$

Martin and Kipping [2] prepared diethyl silicon dichloride in order to see if when decomposed with water a hydrol, $(C_2H_5)_2Si(OH)_2$, was formed, corresponding to dibenzylsilicanediol. It was found, however, that the silicone, $(C_2H_5)_2SiO$, was formed, which then polymerised, giving a compound with a high molecular weight; the body was not analogous to the corresponding ketone.[3] The oxide is a syrup, insoluble in water, sparingly soluble in alcohol and easily soluble in ether. It does not solidify at −15° C., and distils below 300° C. without decomposition.

Alkyl Derivatives of the Type R.SiO.OH.

Methylsiliconic acid or **Silico-acetic acid,** $CH_3.SiO.OH$.—This compound is obtained [4] in the following manner: Tetraethoxysilicon, 15 grams, and 10 grams of zinc methyl are heated in a sealed tube to 120° C., opening the tube at various intervals to allow escape of gases. The final heating should reach 300° C., and the liquid is then fractionated. Methyl triethoxy silicon or orthosilicoacetic acid triethyl ester, B.pt. 146° to 151° C., is thus formed:

$$Si(OC_2H_5)_4+Zn(CH_3)_2=CH_3Si(OC_2H_5)_3+ZnCH_3(OC_2H_5)$$

This is then decomposed by aqueous ammonia or by boiling with hydrogen iodide, B.pt. 127° C., giving methylsiliconic acid, which is a white, amorphous powder, leaving a residue of silica when burned.

Ethylsiliconic acid or **Silico-propionic acid** is obtained from ethyl triethoxy silicon [5] using benzoyl chloride at 300° C.:

$$SiC_2H_5(OC_2H_5)_3+3C_6H_5COCl=C_2H_5SiCl_3+3C_6H_5COOC_2H_5$$

The trichloride is decomposed by water, giving the acid and hydrogen

[1] Taurke, *Ber.*, 1905, 38, 1661.
[2] Martin and Kipping, *Trans. Chem. Soc.*, 1909, 95, 302.
[3] Robison and Kipping, *Trans. Chem. Soc.*, 1908, 93, 439.
[4] Ladenburg, *Annalen*, 1874, 173, 143.
[5] Ladenburg, *ibid.*, 1872, 164, 300.

chloride. Ethyl triethoxy silicon or ethyl trimethoxy silicon with hydrogen iodide or aqueous ammonia yields ethylsiliconic acid:[1]

$$C_2H_5Si(OC_2H_5)_3+3HI=C_2H_5.SiO.OH+3C_2H_5I+H_2O$$

This equation represents the most convenient method of preparation.[2] It may also be isolated when Nordhausen sulphuric acid reacts with triethylsilicol:

$$(C_2H_5)_3Si(OH)+SO_3=C_2H_5SiO.OH+2C_2H_4+H_2+SO_2$$

The acid is an amorphous powder.

Propylsiliconic acid or Silico-butyric acid is produced by allowing propylsilicon trichloride to drop into ice-water.[3] It is insoluble in the usual solvents, and is a hard, solid mass, which can be ground into a powder which is infusible.

Isoamylsiliconic acid or Silico-hexoic acid is prepared in the same way as the above body. It is a hard, brittle solid, with no definite melting-point, and is easily soluble in alcoholic potassium hydroxide, ether, benzene, or chloroform, but is sparingly soluble in alcohol.

Alkyl Derivatives of the Type $R_3Si—SiR_3$.

Hexamethylsilicoethane[4] is formed from silicon hexachloride, Si_2Cl_6, by methyl magnesium bromide. It boils at 112° to 114° C.

Hexaethylsilicoethane[5] is prepared by the interaction of silicon, hexa-iodide and zinc diethyl. It is a liquid, B.pt. 250° to 253° C., having a density of 0·8510 at 0° C. and 0·8403 at 20° C.

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Aromatic Derivatives.

Table I. on next page shows the modes of passing from one compound to another, using the phenyl derivatives as examples.

Table II. shows the condensation products obtained from *diphenylsilicanediol*, and similar compounds are obtained from dibenzylsilicanediol.

Aryl Derivatives of the Type R_4Si.

Tetraphenylsilicane, $(C_6H_5)_4Si$.[6]—This is prepared according to the equation,

$$SiCl_4+4C_6H_5Cl+8Na=Si(C_6H_5)_4+8NaCl$$

in the following manner. Sodium granules, 23 grams, are slowly added to 20 grams of silicon tetrachloride, 56·2 grams of chlorobenzene and a little ethyl acetate in anhydrous ether. It is necessary to cool during the reaction, and after shaking several hours the deep blue powder is filtered off and washed with dry ether. Four-fifths of the filtrate is then distilled off, and a white, crystalline powder obtained, which after

[1] Ladenburg, *Ber.*, 1872, 5, 1081.
[2] Ladenburg, *Ann. Pharm.*, 1872, 164, 300.
[3] Melzer, *Ber.*, 1908, 41, 3390.
[4] Bygdén, *Ber.*, 1912, 45, 707.
[5] Friedel and Ladenburg, *Ann. Chim. Phys.*, 1880, [5], 19, 401; *Annalen*, 1880, 203, 251.
[6] Polis, *Ber.*, 1885, 18, 1540.

TABLE I.

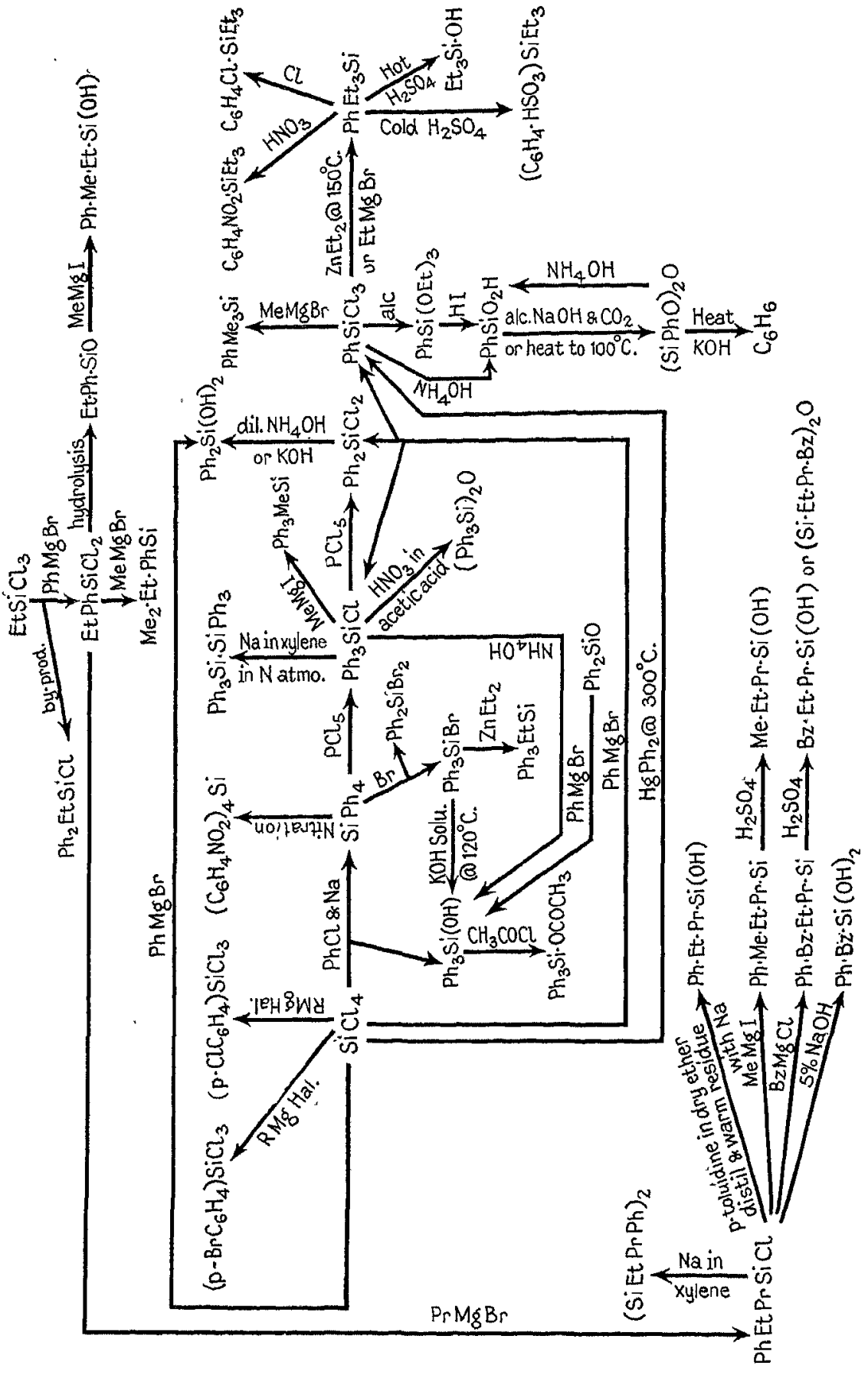
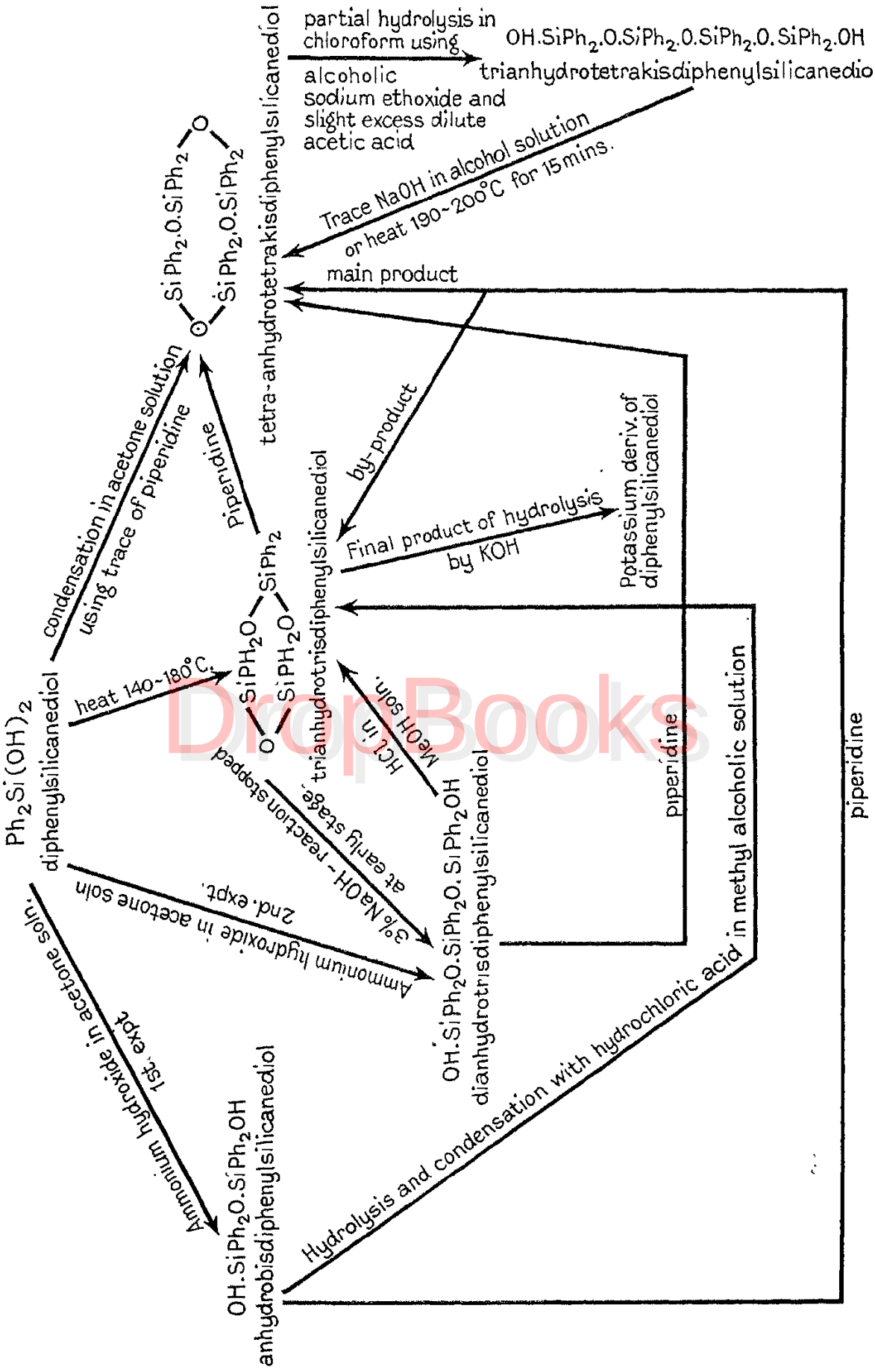

EtSiCl3
PhMgBr
by-prod.
Ph2EtSiCl
Et.PhSiCl2
hydrolysis
Et·Ph·SiO
MeMgI
Ph·Me·Et·Si(OH)2
MeMgBr
Me2·Et·PhSi
PhMgBr
Ph2Si(OH)2
dil. NH4OH or KOH
Ph2SiCl2
PhMe3Si
MeMgBr
PhSiCl3
alc
PhSi(OEt)3
HI
PhSiO2H
NH4OH
alc. NaOH & CO2 or heat to 100°C.
(SiPhO)2O
Heat KOH
C6H6
ZnEt2 @ 150°C. or Et MgBr
Cl
HNO3
C6H4Cl·SiEt3
C6H4NO2SiEt3
PhEt3Si
Hot H2SO4
Et3Si·OH
Cold H2SO4
(C6H4·HSO3)SiEt3
Ph3MeSi
MeMgBr
PCl5
Ph2SiCl2
HNO3 in acetic acid
(Ph3Si)2O
Ph3Si·SiPh3
Na in xylene in N atmo.
Ph3SiCl
HO4HN
Ph2SiO
Ph MgBr
HgPh2 @ 300°C.
PCl5
Ph2SiBr2
Br
Ph3SiBr
ZnEt2
Ph3EtSi
Nitration
SiPh4
KOH Solu. @ 120°C.
Ph3Si(OH)
CH3COCl
Ph3Si·OCOCH3
(C6H4NO2)4Si
PhCl & Na
(C6H4NO2)SiCl3
RMgHal
SiCl4
(p-BrC6H4)SiCl3
(p·ClC6H4)SiCl3
RMgHal.
PhMgBr
PrMgBr
(SiEtPrPh)2
Na in xylene
PhEtPrSiCl
p-toluidine in dry ether distil & warm residue with Na
MeMgI
BzMgCl
5% NaOH
Ph·Et·Pr·Si(OH)
Ph·Me·Et·Pr·Si
Ph·Bz·Et·Pr·Si
H2SO4
H2SO4
Me·Et·Pr·Si(OH)
Bz·Et·Pr·Si(OH) or (Si·Et·Pr·Bz)2O
Ph·Bz·Si(OH)2

TABLE II.



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washing with hot water and drying is crystallised from benzene.[1] The compound belongs to the tetragonal system. It melts at 233° C., and boils without decomposition above 530° C. It has a density of 1·078 at 20° C. In the above preparation of silicon tetraphenyl a by-product is produced in small quantities,[2] M.pt. 148° C., and this is triphenylsilicol, identical no doubt with that from the decomposition of triphenylchlorosilicane with water, M.pt. 139° to 141° C.[3]

Tetra-p-tolylsilicane, $Si(C_6H_4CH_3)_4$, is produced in the same way as silicon tetraphenyl, but using p-bromotoluene. It forms colourless, transparent crystals, M.pt. 228° C., density 1·0793 at 20° C., readily soluble in hot benzene and sparingly soluble in chloroform or ether.

Tetra-m-tolylsilicane is similarly prepared from m-bromotoluene.[3] It forms long prisms, M.pt. 150·8° C., density 1·1188 at 20° C.

Tetrabenzylsilicane is prepared by using benzyl chloride. The reaction is not so vigorous as with chlorobenzene, and after some time the product is warmed on a water-bath before filtering. After washing the residue with dry ether and distilling off the latter, a fuming oil remains, which when treated with ligroin yields a white, crystalline powder. This is recrystallised from warm ether and melts at 127·5° C. It is easily soluble in benzene or chloroform, fairly soluble in warm ether, but sparingly soluble in alcohol. The yield is not so good as in the case of the preceding compounds, dibenzyl being produced, and probably a benzyl silicon chloride, B.pt. 160° to 180° C. Tetrabenzylsilicane distils unchanged above 550° C.

Tetranitrophenylsilicane[3] is prepared by nitrating silicon tetraphenyl. Ten parts of this compound are cooled in ice and salt mixture and 60 parts of fuming nitric acid with 80 parts of concentrated sulphuric acid slowly added in small quantities. The product is filtered through glass-wool, then poured into a large volume of water while stirring. A snow-white precipitate is formed which is dried in the air at room temperature. When dry it is a pale yellow compound, M.pt. 93° to 105° C., easily soluble in benzene, chloroform, or hot acetic acid, and insoluble in alcohol or light petroleum. It explodes above its melting-point.

Triphenylmethylsilicane[4] is prepared by the action of magnesium methyl iodide on triphenylsilicon chloride, and heating the product at 130° C. for three hours. It is recrystallised from petroleum ether and melts at 67° to 67·5° C.

Phenyltrimethylsilicane[5] is obtained from phenyl silicon trichloride by interaction with methyl magnesium bromide, and boils at 171·5° to 171·7° C. It is a transparent, highly refractive liquid, with a characteristic odour.

Benzyltrimethylsilicane occurs from the interaction of benzyltrichlorosilicane and methyl magnesium bromide. It boils at 191·2° to 191·4° C., is isomeric with phenyldimethylethylsilicane and is a colourless liquid, having a strong odour resembling anisole.[5]

[1] Polis, *Ber.*, 1886, 19, 1012.
[2] Kipping and Lloyd, *Proc. Chem. Soc.*, 1899, 15, 174; *Trans. Chem. Soc.*, 1901, 79. 449.
[3] Polis, *loc. cit.*
[4] Marsden and Kipping, *Trans. Chem. Soc.*, 1908, 93, 198.
[5] Bygdén, *Ber.*, 1912, 45, 707.

Triphenylethylsilicane is formed by the action of zinc ethyl on triphenylsilicon bromide.[1] Two products are formed, triphenylethylsilicane and triphenylsilicane; the first is soluble in cold acetone, and the second soluble only with difficulty. Triphenylethylsilicane forms plates, M.pt. 72° to 74° C.[2] It may also be prepared from triphenylsilicon chloride, using excess of ethyl magnesium bromide.[3]

Phenyltriethylsilicane[4] is produced when phenylsilicon trichloride and zinc ethyl, in equal quantities, are heated in a sealed tube for one hour at 150° C. The gas pressure in the tube is then released and the heating continued at 160° C. and finally at 165° C. After treating the product with water, and then hydrochloric acid, an oil is formed which is taken up in ether, washed, dried, and distilled. The product, B.pt. 230° C., is phenyltriethylsilicane, a colourless, faintly fuming liquid, soluble in ether and insoluble in water. It burns with a sooty flame and has a density of 0·9042 at 0° C. **Diphenyldiethylsilicane**, B.pt. 305° to 315° C., is formed as a by-product:

$$2Si(C_2H_5)_3(C_6H_5)=(C_6H_5)_2Si(C_2H_5)_2+Si(C_2H_5)_4$$

Phenyltriethylsilicane gives the following reactions:—[5]

1. $C_6H_5Si(C_2H_5)_3+HNO_3=C_6H_4NO_2.Si(C_2H_5)_3+H_2O$
2. $C_6H_5Si(C_2H_5)_3+H_2SO_4=C_6H_4HSO_3.Si(C_2H_5)_3+H_2O$
3. $C_6H_5Si(C_2H_5)_3+H_2SO_4 \xrightarrow{\text{Hot.}} (C_2H_5)_3SiOH+C_6H_5.SO_3H$
4. $C_6H_5Si(C_2H_5)_3+Cl_2=C_6H_4Cl.Si(C_2H_5)_3+HCl$

The above chlorine substitution product (4) boils at 260° to 265° C., density 1·0185 at 0° C., is insoluble in water, has a faintly aromatic odour, and burns with a green flame, leaving a deposit of silica.[6]

Diphenyldimethylsilicane is obtained by acting upon dichlorodiphenylsilicane with an excess of magnesium methyl iodide. It boils at 176° to 178° C. at 45 mm.[7]

p-Bromophenyltriethylsilicane[8] is formed from ethyl magnesium bromide and p-bromophenyl silicon trichloride. It boils at 149° C. at 14 mm., and has a density of 1·1643 at 21° C. The magnesium compound of the silicane reacts with acetaldehyde and higher aldehydes to form derivatives of the type $Si(C_2H_5)_3.C_6H_4.CHR.OH$ (see Appendix, Table VIA).[9]

p-Chlorophenyltriethylsilicane[10] is prepared as above. It is a colourless, faintly fuming oil, B.pt. 137° C. at 14·5 mm.; density 0·9971 at 18° C.

[1] Ladenburg, *Ber.*, 1907, 40, 2274.
[2] Marsden and Kipping, *Trans. Chem. Soc.*, 1908, 93, 198.
[3] Marsden and Kipping described the compound as forming rhomboidal prisms, M.pt. 76° C., soluble in ether, chloroform, benzene, ethyl acetate, acetone, or light petroleum, moderately soluble in alcohol and insoluble in water.
[4] Friedel and Ladenburg, *Annalen*, 1871, 159, 259.
[5] Ladenburg, *Annalen*, 1874, 173, 160.
[6] Bygdén (*Ber.*, 1912, 45, 707) obtained phenyltriethylsilicane from phenylsilicon trichloride and 4·2 mols. of ethyl magnesium bromide, and found its boiling-point to lie between 238·2° and 238·4° C.
[7] Kipping, *J. Chem. Soc.*, 1927, p. 104.
[8] Grüttner and Krause, *Ber.*, 1917, 50, 1559.
[9] Grüttner and Cauer, *Ber.*, 1918, 51, 1283.
[10] Bygdén, *loc. cit.*

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p-Iodophenyltriethylsilicane is formed from the magnesium compound of p-bromophenyltriethylsilicane, $(C_2H_5)_3Si.C_6H_4.MgBr$, by the action of iodine. It boils at 165° C. at 13 mm.; density 1·3342 at 16° C.

p-Chlorophenyltri-n-propylsilicane is obtained from p-chlorophenylsilicon trichloride and n-propyl magnesium chloride. It is an oil with a faint odour, B.pt. 160° C. at 14 mm.; density 0·9663 at 14° C.

The refractivities of the above compounds are shown in Table VI. of the Appendix.

Phenyldimethylethylsilicane, $(CH_3)_2(C_2H_5)(C_6H_5)Si$,[1] is best prepared from phenylethylsilicon dichloride, which is obtained according to the equation:

$$\underset{(1\ \text{mol.})}{C_2H_5SiCl_3} + \underset{(1{\cdot}1\ \text{mol.})}{C_6H_5MgBr} = (C_2H_5)(C_6H_5)SiCl_2 + MgClBr$$

By the action of methyl magnesium bromide on the above dichloride, the desired silicane is produced, B.pt. 197·6° to 198·6° C. The product is not quite pure.

Benzylethyldipropylsilicane [2] is obtained from benzylethylpropylsilicon chloride by the action of magnesium propyl bromide. It boils at 280° C., and is a colourless, mobile liquid. It is converted into benzylethyldipropylsilicane sulphonic acid, $(C_2H_5)(C_3H_7)_2.Si.CH_2.C_6H_4.SO_3H$, by chlorosulphonic acid in chloroform solution. The *l-menthylamine salt*, $Si.C_2H_5(C_3H_7)_2CH_2.C_6H_4SO_3H.C_{10}H_{19}NH_2$, prepared from the ammonium salt, is a colourless solid. The *cinchonidine salt* melts at 194° to 195° C., and has the value $[\alpha]_D$ −72°. The *cinchonidine hydrogen salt* melts at 222° to 224° C. The *quinine salt* has a melting-point of 175° C., and $[\alpha]_D$ −112·3°. The *quinine hydrogen salt* melts at 223° to 224° C. The *l*-menthylamine, cinchonidine, and quinine salts are very similar to the corresponding salts of *dl*-benzylmethylethylpropylsilicane sulphonic acid, which seems to point to the fact that the latter are merely mixtures of their optically isomeric components.

Dibenzylethylpropylsilicane [3] is prepared by the interaction of benzylethylpropylsilicon chloride and magnesium benzyl chloride. The body is easily acted on by chlorosulphonic acid, like all silicon hydrocarbons containing a benzyl group. Sulphonation under suitable circumstances gives a mono acid which is usually accompanied by a disulphonic acid. Dibenzylethylpropylsilicane is a colourless liquid, lighter than water. It is miscible with most organic solvents, and has a violet fluorescence. The *l-menthylamine salt*,

$$C_6H_5CH_2.Si.C_2H_5.C_3H_7.CH_2.C_6H_4.SO_3H.C_{10}H_{19}NH_2.2H_2O$$

crystallises from moist petroleum ether in plates, and is similar to the corresponding salt of the monosulphonic derivatives of benzylmethylethylpropylsilicane.

Phenylmethylethylpropylsilicane [4] is produced by the action of methyl magnesium iodide on phenylethylpropylsilicon chloride. It is a mobile liquid, B.pt. 228° to 230° C., and is decomposed by sulphuric acid, giving apparently benzene and methylethylpropylsilicol.

[1] Bygdén, *Ber.*, 1912, 45, 707.

[2] Marsden and Kipping, *Proc. Chem. Soc.*, 1908, 24, 12; *Trans. Chem. Soc.*, 1908, 93, 198.

[3] Challenger and Kipping, *Trans. Chem. Soc.*, 1910, 97, 142.

[4] Kipping, *Proc. Chem. Soc.*, 1905, 21, 65; *Trans. Chem. Soc.*, 1907, 91, 209.

Phenylbenzylethylpropylsilicane is prepared by the action of the benzyl Grignard reagent on phenylethylpropylsilicon chloride. The compound is a colourless, highly refractive liquid, lighter than water, B.pt. 249° to 251° C. at 100 mm., and is readily decomposed by sulphuric acid, giving benzene and benzylethylpropylsilicol or the corresponding ether, $(Si.C_2H_5.C_3H_7.C_6H_5CH_2)_2O$. When this decomposition product of phenylbenzylethylpropylsilicane is heated with sulphuric acid it undergoes sulphonation, but only one acid of the several formed has been separated. It seems to have the composition

$$Si.C_2H_5.C_3H_7.OH.CH_2.C_6H_4.SO_3H$$

Benzylmethylethylpropylsilicane is prepared in the same way as the corresponding phenyl compound, using methyl magnesium iodide and benzylethylpropyl silicon chloride.[1] It is a mobile liquid, B.pt. 177° C. at 100 mm. Sulphuric acid at 130° C. sulphonates the body, forming a mixture of acids, two of which have been separated in the form of their *l-menthylamine salts*. Analysis apparently points to one being derived from benzylethylpropylsilicolsulphonic acid, and therefore its formula is

$$C_2H_5.C_3H_7.Si(OH).CH_2C_6H_4.SO_3H.C_{10}H_{19}NH_2$$

Being only produced in small quantity, it has not been very thoroughly investigated. The salt crystallises in prisms, M.pt. 210° to 212° C. The second *l-menthylamine salt* has the composition,

$$Si(CH_3)(C_2H_5)(C_3H_7)CH_2.C_6H_4.SO_3H.C_{10}H_{19}NH_2$$

and can be more readily formed by sulphonation of benzylmethylethylpropylsilicane with chlorosulphonic acid. It crystallises with 2 mols. of water of crystallisation from wet petroleum ether, and the dehydrated salt melts at 122·3° C. The *l-menthylamine, quinine, cinchonidine, cinchonine, narcotine,* and several other salts of the above *dl*-silicane sulphonic acid have been fractionally crystallised under different conditions, but no indication of resolution of the acid has been observed.

Benzylethylpropylisobutylsilicane[2] is obtained from benzylethylpropylsilicon chloride by isobutyl magnesium bromide, and is a colourless liquid resembling a hydrocarbon, B.pt. 282° to 283° C. It is sulphonated by chlorosulphonic acid, as in the case of the previous compound containing more closely related groups, and the *l-menthylamine salt* obtained. After fractionally crystallising this it cannot be resolved. Several other salts have been made using active bases. The extreme fractions of the hydrogen salts of *quinine, cinchonine,* and *cinchonidine* have been investigated, but, except for the last case, the melting-points and specific rotations of these fractions of a given salt are identical within limits of experimental error. In the *cinchonidine hydrogen salt* two fractions investigated are thus: most readily soluble fraction, $[\alpha]_D$ +61·6°; sparingly soluble, $[\alpha]_D$ +72·7°. One crystallisation from ethyl acetate and methyl alcohol gives results +57·1° and 73·8°, and the decomposition points of the fractions are then identical (220° to 223° C.). The next most readily soluble fraction gives +62·5°, and the decomposition point is the same as the above.

[1] Kipping, *Proc. Chem. Soc.*, 1905, 21, 65; 1907. 23, 83; *Trans. Chem. Soc.*, 1907, 92, 717.

[2] Kipping and Davies, *Proc. Chem. Soc.*, 1909, 25, 9; *Trans. Chem. Soc.*, 1909, 95, 68.

Further results have failed to show resolution. Possibly they are resolved under certain conditions, but the enantiomorphous relationship between the two optically active acids is difficult to establish.

Aryl Derivatives of the Type R_3SiX.

Triphenylchlorosilicane, $(C_6H_5)_3SiCl$, is prepared [1] from tetraphenylsilicane and phosphorus pentachloride:

$$(C_6H_5)_4Si+PCl_5=(C_6H_5)_3SiCl+C_6H_5Cl+PCl_3$$

It forms colourless crystals, fuming slightly in air, M.pt. 88° to 89° C. This substance may be distilled under reduced pressure without decomposition, but hydrogen chloride is evolved when it is distilled at the ordinary pressure. It is readily soluble in light petroleum, anhydrous ether, benzene, chloroform, or carbon bisulphide, but in absolute alcohol it yields the corresponding *ester*. The chloro-compound undergoes rupture at the phenyl-silicon linking when treated with metallic sodium in liquid ammonia. Triphenylchlorosilicane combines with 2 mols. of ammonia, giving a product which on decomposition yields *triphenylsilicylamine*, M.pt. 55° to 56° C.[2]

Triphenylbromosilicane [3] is obtained by warming tetraphenylsilicane with the molecular quantity of bromine on a water-bath, then 10 per cent. bromine is added and the whole heated to 150° C. for eight or ten hours.

$$(C_6H_5)_4Si+Br_2=(C_6H_5)_3SiBr+C_6H_5Br$$

The residue is treated with ligroin, the solvent distilled off, and the bromobenzene removed *in vacuo*, when impure bromide remains. It forms colourless, small needles, fuming slightly in air, M.pt. 118° to 120° C., and is easily decomposed by water or alcohol. It is readily dissolved by ether or hot benzene, but is difficultly soluble in ligroin. The yield is about 30 per cent.

Triphenylsilicon acetate, $(C_6H_5)_3Si.OCOCH_3$, is produced by boiling triphenylsilicol with acetyl chloride.[4] It forms colourless prisms, M.pt. 91° to 92° C.

Tribenzylchlorosilicane [5] crystallises in prisms, M.pt. 141° C., B.pt. 300° to 360° C. at 100 mm. Water decomposes it into tribenzylsilicol.

Diphenylethylchlorosilicane is obtained by working up the by-product, B.pt. above 240° C., in the preparation of phenylethylsilicon dichloride, which is isolated from phenyl magnesium bromide and ethyl silicon trichloride. It is a colourless liquid, B.pt. 206° to 208° C. at 50 mm. The corresponding *methyl* compound boils at about 180° to 195° C.

Dibenzylethylchlorosilicane occurs in the preparation of benzylethyl silicon dichloride, using benzyl magnesium chloride on ethyl silicon trichloride.[6] It is a colourless oil, fuming in moist air, and is

[1] Polis, *Ber.*, 1886, 19, 1012.
[2] Kraus and Rosen, *J. Amer. Chem. Soc.*, 1925, 47, 2739.
[3] Ladenburg, *Ber.*, 1907, 40, 2274.
[4] Kipping and Lloyd, *Proc. Chem. Soc.*, 1899, 15, 174; *Trans. Chem. Soc.*, 1901, 79, 449.
[5] Marsden and Kipping, *Proc. Chem. Soc.*, 1908, 24, 25; Martin and Kipping, *Trans. Chem. Soc.*, 1909, 95, 302.
[6] Kipping, *Proc. Chem. Soc.*, 1905, 21, 65; Challenger and Kipping, *Trans. Chem. Soc.*, 1910, 97, 142.

decomposed by water into the silicol, this spontaneously passing into the *compound* $[(C_6H_5CH_2)(C_2H_5)Si]_2O$, M.pt. 56° C., when kept over sulphuric acid for a time.

Phenylethylpropylchlorosilicane [1] is the principal product from the interaction of phenylethylsilicon dichloride and propyl magnesium bromide. Its boiling-point is not very definite (about 250° to 260° C.), and it is a colourless, refractive, mobile liquid, fuming in air, and readily decomposed by water.

Benzylethylpropylchlorosilicane is produced from benzylethylsilicon dichloride (1 mol.) and propyl magnesium bromide (1 mol.). It is a colourless, fuming, mobile liquid, which generally becomes pink, and is immediately decomposed by water, yielding the corresponding silicol and oxide. It boils at 172° to 176° C. at 50 mm., and the yield is 50 to 60 per cent. of the theoretical.

Benzylethylisobutylchlorosilicane.[2]—By the action of isobutyl magnesium bromide on benzylethyl silicon dichloride the above compound is produced. It has the same properties as the preceding body, and boils at 198° to 202° C.

Aryl Derivatives of the Type R_2SiX_2.[3]

Diphenylsilicon dichloride [4] is obtained from triphenylchlorosilicane and phosphorus pentachloride. It is a colourless liquid, B.pt. 230° to 237° C. at 90 mm. It also occurs by the interaction of silicon tetrachloride and phenyl magnesium bromide.[5] Silicon tetrachloride (170 grams) is stirred, cooled to 0° C. and 2·25 mols. of phenyl magnesium bromide in ether very slowly added. After allowing the whole to stand for twelve hours with occasional shaking, it is refluxed for three hours, then filtered in the absence of moisture [6] and washed with ether. The ether is removed by distillation, and after standing half an hour the remaining oil is refiltered and distilled at 50 mm. Three fractions are obtained :

1. 110° to 120° C., phenyl silicon trichloride.
2. 190° to 225° C., diphenyl silicon dichloride.
3. 260° to 300° C., triphenyl silicon chloride.

Fraction 2 on redistilling gives a colourless oil, fuming slightly in moist air, B.pt. 202° to 204° C. at 45 mm.

[1] Kipping, *Proc. Chem. Soc.*, 1904, 20, 15 ; 1905, 21, 65 ; *Trans. Chem. Soc.*, 1907, 91, 209.

[2] Luff and Kipping, *Proc. Chem. Soc.*, 1908, 24, 224 ; *Trans. Chem. Soc.*, 1908, 93, 2004.

[3] A possible impurity in diphenylsilicon dichloride may be diethoxydiphenylsilicane (Kipping, *J. Chem. Soc.*, 1927, p. 2734), and the B.pt. of the latter compound differs little from that of the dichloride, as seen from the following figures :—

$SiPh_2(OEt)_2$, 197° to 198° C. at 50 mm. ; 217° to 218° C. at 100 mm. ; 302° to 304° C. at 767 mm. $SiPh_2Cl_2$, 199° to 202° C. at 50 mm. ; 222° to 224° C. at 100 mm. ; 302° to 305° C. at 767 mm. The silicane is specifically heavier than water and miscible in common solvents. An alcoholic solution in the presence of a little alkali yields trianhydrotrisdiphenylsilicanediol, and it is also slowly hydrolysed by dilute sulphuric acid.

[4] Polis, *Ber.*, 1886, 19, 1012.

[5] Dilthey and Eduardoff, *Ber.*, 1904, 37, 1139 ; Kipping, *Trans. Chem. Soc.*, 1912, 101, 2108 ; see Kipping and Murray, *J. Chem. Soc.*, 1927, p. 2737.

[6] Kipping, *Trans. Chem. Soc.*, 1907, 91, 216.

By the action of mercuric oxide on this compound, an *oxide*, $[SiPh_2O]_n$, has been obtained.[1]

Diphenyl silicon dibromide.[2]—In the preparation of triphenylbromosilicane from tetraphenylsilicane and bromine the above compound is also formed. It boils between 175° and 183° C. at 12 mm.

Dibenzyl silicon dichloride.[3]—In the preparation of benzylethyl silicon dichloride an oily by-product is formed, which in addition to dibenzyl and other silicon compounds contains dibenzyl silicon dichloride. It melts at 50° to 52° C., fumes in air, and decomposes with water, giving the diol. By mercuric oxide it is transformed to a *polymerised form* of $SiBz_2O$, soluble in ether, acetone, or benzene.[4]

Phenylethyl silicon dichloride is prepared from ethyl silicon trichloride and phenyl magnesium bromide. It boils at 228° to 232° C. and is a highly refractive liquid, fuming strongly in moist air.

Benzylethyl silicon dichloride is obtained as above, using the benzyl Grignard reagent. To avoid formation of too much dibenzyl, the reaction is carried out at 0° C. The two products obtained are benzylethyl silicon dichloride and *dibenzylethyl silicon chloride*. The former is a mobile, fuming liquid, B.pt. 169° C. at 100 mm.

Aryl Derivatives of the Type $RSiX_3$.

Phenyl silicon trichloride.—This compound is made from silicon tetrachloride and mercury diphenyl.[5] The two are heated at 300° C. in sealed tubes and the product fractionally distilled. The trichloride is a colourless liquid, B.pt. 197° to 198° C.; it fumes in air and is slowly decomposed in cold water, more rapidly on warming or addition of ammonium hydroxide. It burns with a sooty flame, depositing silica:

$$SiCl_4 + Hg(C_6H_5)_2 = C_6H_5SiCl_3 + C_6H_5HgCl$$

Kipping prepared the body using the Grignard reagent.[6] One molecule of silicon tetrachloride and 1·25 mols. of phenyl magnesium bromide are used, and the experiment carried out as for diphenyl silicon dichloride. The crude body is collected between 110° and 120° C. at 50 mm. and purified by repeated distillation under reduced pressure. Fifty grams of trichloride, B.pt. 198° to 200° C., are obtained from 120 grams of silicon tetrachloride. The compound is hydrolysed by ice-cold water or ammonium hydroxide solution,[7] and the results seemed to point to the formation of condensation products, similar to those of the diarylsilicanediols, and not phenylsiliconic acid, $C_6H_5SiO_2H$, by elimination of water from $C_6H_5Si(OH)_3$. This view supports the possibility that the so-called siliconic acids are merely mixtures. At lower temperatures, the products of hydrolysis are possibly largely condensation products of the composition $C_6H_5SiO_2H$ or $xC_6H_5Si(OH)_3 - xH_2O$, and at ordinary temperatures higher condensation products are formed

[1] Vyle and Kipping, *Trans. Chem. Soc.*, 1924, 125, 2616.
[2] Ladenburg, *Ber.*, 1907, 40, 2274.
[3] Robison and Kipping, *Trans. Chem. Soc.*, 1908, 93, 439; Martin and Kipping, 1909, 95, 302.
[4] Vyle and Kipping, *loc. cit.*
[5] Friedel and Ladenburg, *Annalen*, 1871, 159, 259; Ladenburg, *Ber.*, 1873, 6, 379.
[6] Kipping, *Trans. Chem. Soc.*, 1912, 101, 2106; Meads and Kipping, *Trans. Chem. Soc.*, 1914, 105, 679.
[7] Meads and Kipping, *ibid.*

approximating to the formula $(C_6H_5SiO)_2O$. For derivatives from the trichloride and magnesium p-bromophenyl bromide (see Appendix, Table VIA).[1]

p-Chlorophenyl-silicon trichloride[2] is obtained from silicon tetrachloride and the magnesium compound of p-chlorobromobenzene. It is a colourless oil, B.pt. 105° C. at 15 mm., and is hydrolysed by water to the "so-called siliconic acid," an amorphous powder.

p-Bromophenyl silicon trichloride is similarly prepared from the magnesium compound of p-dibromobenzene and silicon tetrachloride. It is a faintly fuming oil, B.pt. 120° to 125° C., and is also hydrolysed by water. With alcohol it forms esters of the type $C_6H_4.Br.Si(OR)_3$ (see Appendix, Table VIA).[3]

p-Tolyl silicon trichloride.[4]—Tetrachloro-silicane and mercury di-p-tolyl are heated in sealed tubes at 300° to 320° C., when the above compound occurs as a strongly refractive, fuming liquid, B.pt. 218° to 220° C. It is found to be decomposed by water, giving a *compound* having the apparent composition $C_7H_7SiO_2H$, and this when heated at 200° C. seems to be transformed into the *oxide*, $(C_7H_7SiO)_2O$.

Benzyl silicon trichloride[5] is produced when benzyl magnesium chloride is allowed to interact with silicon tetrachloride. It is a transparent, strongly fuming liquid, with a powerful odour, density 1·2834, B.pt. 94° to 96° C. at 11 mm.

α-Naphthyl silicon trichloride is produced in the above manner and is similar to the preceding compound, density 1·3760, B.pt. 165° to 170° C. at 22 mm.

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Aryl Derivatives of the Type $R_3Si(OH)$.

Triphenylsilicol, $(C_6H_5)_3Si(OH)$,[6] is formed from triphenylchloro-silicane by boiling with water and a little ammonium hydroxide. It is also produced from the bromide by potassium hydroxide solution at 120° C. It is easily soluble in alcohol, ether, chloroform, or benzene, and may be crystallised from acetone, M.pt. 139° to 141° C. (Polis), 148° to 150° C. (Ladenburg). The compound is also prepared by treating the silicone, $(C_6H_5)_2SiO$, with the Grignard reagent.[7] Prepared thus it crystallises in prisms, M.pt. 150° to 151·5° C. (Marsden and Kipping).

Triphenylsilicol trisulphonic acid, $(C_6H_4SO_3H)_3Si(OH)$, is made by gently warming one part of the above silicol with six parts of fuming sulphuric acid. When it is all dissolved, the solution is poured into cold water, neutralised with barium carbonate, then gently warmed and filtered from barium sulphate. Evaporation of the filtrate yields the *barium salt* in white flakes.

Trisulphonate of trinitrophenylsilicol.—The above compound is nitrated, using five parts of fuming nitric acid, whilst strongly cooling

[1] Grüttner and Cauer, *Ber.*, 1918, 51, 1283.
[2] Grüttner and Krause, *Ber.*, 1917, 50, 1559.
[3] Grüttner and Cauer, *loc. cit.*
[4] Ladenburg, *Annalen*, 1874, 173, 160; *Ber.*, 1874. 27, 803.
[5] Melzer, *Ber.*, 1908, 41, 3390; Martin and Kipping, *Trans. Chem. Soc.*, 1909, 95, 302.
[6] Polis, *Ber.*, 1886, 19, 1012; Ladenburg, *Ber.*, 1907, 40, 2274.
[7] Kipping and Lloyd, *Proc. Chem. Soc.*, 1899, 15, 174; Marsden and Kipping, *Trans. Chem. Soc.*, 1908, 93, 198.

the mixture. The product is poured into cold water, partly evaporated to remove some of the nitric acid, then again diluted and neutralised with barium carbonate. An intense yellow solution is formed, this after filtration and evaporation yielding the *barium salt* of the compound as yellow crusts, which are recrystallised from water.

Phenylmethylethylsilicol.[1]—Phenylethylsilicone is first prepared from phenylethyl silicon dichloride by hydrolysis, and the silicone then allowed to interact with methyl magnesium iodide. The product is contained in the fraction boiling at 115° C. at 17 mm. It is a colourless, mobile liquid, practically insoluble in water, and on standing slowly passes to the oxide which produces a turbidity.

Phenyldiethylsilicol is also prepared from the silicone, as in the case of the previous compound. It boils at 165° C. at 60 mm. With water it is slowly decomposed, probably yielding phenyldiethylsilicyl oxide.

Phenylethylpropylsilicol[2] is formed from phenylethylpropyl silicon chloride by treating it with p-toluidine in dry ether. The ether is distilled off and the residue warmed with sodium, then fractionated. It has similar properties to the above, and boils at 250° C.

Tribenzylsilicol[3] is prepared from benzyl silicon trichloride, which with cold water yields benzyl meta-silicic acid. This, with a large excess of benzyl magnesium chloride, and heating the reaction mixture to 220° C., gives the silicol, the dibenzyl being removed by steam-distillation. The remaining pasty mass is extracted with ether, and the silicol distilled at 250° to 300° C. at 20 mm. The fraction solidifies and is crystallised from chloroform and light petroleum, M.pt. 104° C. The yield is only 5 grams from 14 grams of the acid. It has also been prepared using excess of Grignard reagent,[4] or from tribenzylchlorosilicane using moist alcohol.[5]

Dibenzylmethylsilicol is formed from dibenzylsilicone, M.pt. 98° C., using ethereal methyl magnesium iodide and heating at 200° C. for one hour after distilling off the ether. An oily product is isolated, which mostly distils between 240° and 242° C. at 60 mm.

Dibenzylethylsilicol is obtained also as an oil, and passes spontaneously into *dibenzylethylsilicyl oxide*, M.pt. 54° C.

Benzyldiethylsilicol is isolated from benzylethylsilicone by gradually adding it to the ethyl Grignard reagent (1·5 mols.). The residue is finally heated to 190° C. for an hour, then treated when cold with water. The oil is extracted with ether, and 60 per cent. comes over at 165° C. at 40 mm. It is a colourless liquid, miscible with most organic solvents and decomposes slowly to oxide, depositing globules of water, and becoming cloudy. With acetyl chloride this silicol does not give the corresponding chloride, as in the case of tribenzylsilicol.

Benzylethylpropylsilicol may be obtained by two methods :

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[1] Kipping and Hackford, *Trans. Chem. Soc.*, 1911, 99, 138.

[2] Kipping, *Trans. Chem. Soc.*, 1907, 91, 209.

[3] Kipping and Hackford, *Proc. Chem. Soc.*, 1911, 27, 8; *Trans. Chem. Soc.*, 1911, 99, 138.

[4] Dilthey and Eduardoff, *Ber.*, 1905, 38, 4132. Dilthey and Eduardoff give the melting-point 106° C., and describe the body as crystallising from alcohol in long, colourless needles.

[5] Robison and Kipping, *Trans. Chem. Soc.*, 1908, 93, 439.

1. By the decomposition of benzylethylpropylchlorosilicane with water.[1] Two products result, one possibly being the ether,

$$(C_6H_5CH_2.C_2H_5.C_3H_7.Si)_2O$$

B.pt. 255° C. at 25 mm., but the principal product is the silicol, B.pt. 155° C. at 25 mm. The silicane used in the preparation is formed from benzylethyldichlorosilicane and propyl magnesium bromide.

2. From benzylethylsilicone, $C_6H_5CH_2.C_2H_5.SiO$, and propyl magnesium bromide. The mixture is heated to 190° C., then decomposed by water.[2]

Benzylethylpropylsilicol is easily sulphonated, giving *two acids* at least. The *ammonium salt* of one seems to show it is derived from the acid of constitution,

$$C_2H_5.C_3H_7.Si(OH).CH_2.C_6H_4SO_3H$$

but molecular weight determinations indicate polymerisation or condensation. Sulphonation of the pure oxide, using chlorosulphonic acid, appears to give similar acids to those obtained from the silicol, the constitution being

$$SO_3H.C_6H_4CH_2.Si(C_2H_5)(C_3H_7)-O-Si(C_2H_5)(C_3H_7).CH_2C_6H_4SO_3H$$

Benzylethylisobutylsilicol[3] is formed when the corresponding chloride is treated with water. It boils at 162° to 164° C. at 25 mm. In each case, when the chloride, oxide, or silicol is sulphonated, the product is a mixture from which the *dl*-acid, *sulphobenzylethylisobutylsilicyl oxide* is isolated as its *l-menthylamine salt*,

$$[Si.C_2H_5.C_4H_9.CH_2.C_6H_4SO_3H]_2O.2C_{10}H_{21}N.4H_2O$$

M.pt. 240° to 245° C. and $[\alpha]_D$ −14·7° in methyl alcohol solution.

Aryl Derivatives of the Type $R_2Si(OH)_2$.

Diphenylsilicanediol and its condensation products have been studied by Kipping with interesting results.[4] It may be prepared from 8 grams of silicon tetrachloride and 17 grams of phenyl magnesium bromide in the following manner:–[5]

During addition of the tetrachloride the mixture is carefully cooled, and then allowed to remain at room temperature until the greenish precipitate does not increase. Then the product is decomposed with ice-water, extracted with ether, and the solvent distilled off. The residue on crystallisation from benzene gives a 25 to 30 per cent. yield of the diol, which forms glistening needles, M.pt. 138° to 139° C. It is easily soluble in ether or chloroform, but sparingly soluble in ligroin.

[1] Kipping, *Proc. Chem. Soc.*, 1905, **21**, 65; *Trans. Chem. Soc.*, 1907, **91**, 717.
[2] Kipping and Hackford, *Trans. Chem. Soc.*, 1911, **99**, 138.
[3] Luff and Kipping, *Proc. Chem. Soc.*, 1908, **24**, 224; *Trans. Chem. Soc.*, 1908, **93**, 2004.
[4] Kipping, *Proc. Chem. Soc.*, 1912, **28**, 243, 244, 245; *Trans. Chem. Soc.*, 1912, **101**, 2108; Kipping and Robison, *Proc. Chem. Soc.*, 1913, **29**, 374; *Trans. Chem. Soc.*, 1914, **105**, 484.
[5] Dilthey and Eduardoff, *Ber.*, 1904, **37**, 1139.

It may be dried at 100° C. without decomposition. Further heating at a higher temperature causes elimination of 1 mol. of water, but the remaining mass is gelatinous and has no definite melting-point, being probably diphenylsilicone, $(C_6H_5)_2SiO$.[1]

The diol is also formed by the action of dilute ammonium hydroxide or water on diphenylsilicon dichloride.[2]

Kipping in 1912 prepared the compound from diphenylsilicon dichloride and water, but it was difficult to obtain it pure. Dilute ammonium hydroxide on the dichloride gives only a small proportion of diphenylsilicanediol. When the dichloride is slowly added to 5 per cent. potassium hydroxide (4 mols.), slight heat is developed, and on feebly acidifying with acetic acid a white paste is formed, which when freshly precipitated is soluble in potassium hydroxide but changed during filtration and no longer soluble.

Some air-dried specimens show a melting-point of 105° to 110° C., effervescence being due to steam. Attempts to purify the diphenylsilicanediol show it to be usually decomposed in ether, or ethyl acetate. Occasionally, however, it has been thrown down from solvents as a lustrous powder or imperfect prisms, and an oil remains in the mother-liquor. The melting-points vary, and this is probably due to traces of acid in the solvents, rather than removal of impurity by them. A trace of hydrochloric acid in a solution of diol usually causes a rise in melting-point to about 145° C. On this account crystallisation is carried out with ether at ordinary temperature, and the ethereal solution allowed to float on water containing a trace of potassium hydroxide. In this case diphenylsilicanediol is obtained as lustrous prisms, completely soluble in potassium hydroxide and decomposed at 115° to 118° C. with effervescence. Another means of purification is to dissolve the compound in acetone, then to dilute with a small proportion of water. The liquid is milky, and after standing a few days the diol separates, and is filtered, the milky liquid going through. The crystals are washed free from oil with chloroform. This operation is repeated until there is no milkiness, and then the pure diol is obtained after one more crystallisation with hot ethyl acetate or acetone.

Diphenylsilicanediol forms long, colourless needles or prisms which often exceed 20 mm. in length. It sinters at 125° C., and becomes liquid with effervescence at 128° to 132° C. It is practically insoluble in water or light petroleum, only sparingly soluble in cold chloroform, and very moderately soluble in boiling benzene. It easily dissolves in hot ether, ethyl acetate, or acetone. The diol is stable at ordinary temperatures, but its isolation is difficult owing to its sensibility towards alkalis, acids, and other reagents. The crystal measurements are shown in Table VII. of Appendix.

Diphenylsilicanediol in the presence of acids or alkalis very easily undergoes condensation. This accounts for the glue-like substances obtained in the preparation of the diol from diphenyl silicon dichloride by various methods, and they consist of a mixture of any of the four following condensation products :—

1. **Anhydrobisdiphenylsilicanediol,**

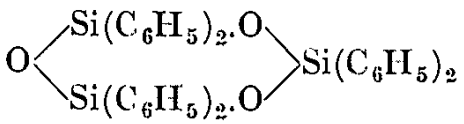
$$HO.Si.(C_6H_5)_2.O.Si(C_6H_5)_2.OH.$$

[1] Kipping and Lloyd, *Trans. Chem. Soc.*, 1901, 79, 449.
[2] Martin, *Ber.*, 1912, 45, 403.

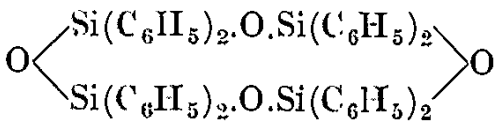
2. **Dianhydrotrisdiphenylsilicanediol,**

$$HO.Si(C_6H_5)_2.O.Si(C_6H_5)_2.O.Si(C_6H_5)_2.OH$$

3. **Trianhydrotrisdiphenylsilicanediol,**



4. **Tetra-anhydrotetrakisdiphenylsilicanediol,**



When diphenylsilicanediol is heated at 140° to 180° C. it loses approximately 1 mol. of water and yields mainly trianhydrotrisdiphenylsilicanediol. In addition, a small amount of tetra-anhydrotetrakisdiphenylsilicanediol is produced, and also an oil, easily soluble in petroleum ether containing a little chloroform. It is proved not to be diphenylsilicone, which at first it seems likely to be, for a small quantity of dianhydrotrisdiphenylsilicanediol is isolated. Steam-distillation gives no diphenylsilicone in the distillate. Part of the oily product appears to consist of anhydrobis- and dianhydrotris- diphenylsilicanediol.

When diphenylsilicanediol undergoes condensation in acetone solution in the presence of a trace of piperidine, crystals of tetra-anhydrotetrakisdiphenylsilicanediol, M.pt. 200° C., are deposited, together with a small amount of a colourless powder, probably a condensation product more complex than the above.

Diphenylsilicanediol in acetone containing a little ammonium hydroxide gives an oil at ordinary temperatures, which, when crystallised from chloroform and light petroleum, yields anhydrobisdiphenylsilicanediol, M.pt. 113° C., and soluble in 5 per cent. potassium hydroxide. Another experiment carried out in the same way gave a compound, M.pt. 112° C., insoluble in potassium hydroxide solution. It was dianhydrotrisdiphenylsilicanediol. The products here are not closed chain condensation bodies.

Anhydrobisdiphenylsilicanediol. The crystals deposited from a mixture of chloroform and light petroleum give the measurements shown in Table VIII. of the Appendix.

The action of piperidine on anhydrobisdiphenylsilicanediol is to give tetra-anhydrotetrakisdiphenylsilicanediol and some trianhydrotrisdiphenylsilicanediol, together with a powder consisting possibly of highly complex condensation products. The action of piperidine, besides causing condensation, also brings about hydrolysis of the anhydrobisdiphenylsilicanediol, giving diphenylsilicanediol, and this then condenses forming a small quantity of trianhydrotrisdiphenylsilicanediol.

Anhydrobisdiphenylsilicanediol changes after a time in the presence of hydrochloric acid in methyl alcohol solution, giving a small quantity of oil. The solvent is allowed to evaporate at ordinary temperature and the process repeated. The oil is washed with alcohol, and the substance when crystallised from ethyl acetate yields prisms of trianhydrotrisdiphenylsilicanediol, M.pt. 188° C. No tetra-anhydro compound is detected. The hydrochloric acid therefore does not cause condensa-

tion, but hydrolyses the anhydrobisdiphenylsilicanediol to the diphenylsilicanediol, which then condenses to give trianhydrotrisdiphenylsilicanediol.

Dianhydrotrisdiphenylsilicanediol, deposited from chloroform and light petroleum, gives the crystal measurements shown in Table IX. of Appendix.

The action of piperidine on dianhydrotrisdiphenylsilicanediol is to give tetra-anhydrotetrakisdiphenylsilicanediol, while some trianhydrotrisdiphenylsilicanediol is probably produced.

Experiments seem to show that piperidine on diphenylsilicanediol, anhydrobis- and dianhydrotris- diphenylsilicanediol give as principal product tetra-anhydrotetrakisdiphenylsilicanediol.

When hydrochloric acid is added to a methyl alcohol solution of dianhydrotrisdiphenylsilicanediol, an oil separates, which on evaporation at the ordinary temperature yields a crystalline residue. Recrystallisation from ethyl acetate gives prisms of trianhydrotrisdiphenylsilicanediol, M.pt. 188° C.

Trianhydrotrisdiphenylsilicanediol, a closed chain compound, is hydrolysed by potassium hydroxide, giving as final product the potassium derivative of diphenylsilicanediol. On evaporating off the alcohol and adding a slight excess of acetic acid to the residue the diol is deposited. The following equation represents the reaction when hydrolysis is stopped at a very early stage of its development :—

$$O\begin{<}{Si(C_6H_5)_2O \atop Si(C_6H_5)_2O}\end{>}Si(C_6H_5)_2 + H_2O = HO.Si(C_6H_5)_2O.Si(C_6H_5)_2.OSi(C_6H_5)_2OH$$

0·25 gram of the trianhydro-compound is dissolved in a mixture of acetone and a little ether, then (0·05 gram) 3 per cent. aqueous sodium hydroxide added. In less than half a minute this is acidified with dilute acetic acid and the solvents evaporated rapidly at the ordinary temperature. The oily residue is next treated with alcohol, filtered, and again evaporated at the ordinary temperature, and the oil after crystallisation from a mixture of chloroform and light petroleum gives pure dianhydrotrisdiphenylsilicanediol.

Trianhydrotrisdiphenylsilicanediol, like the corresponding benzyl compound, is hydrolysed by hydrogen chloride into the open chain compound dianhydrotrisdiphenylsilicanediol. This hydrolysis is reversible. Piperidine on the trianhydrotris-derivative gives tetra-anhydrotetrakisdiphenylsilicanediol mixed with unchanged product.

Crystals of trianhydrotrisdiphenylsilicanediol deposited from ethyl acetate solution have been measured, and the results are shown in Table X. of Appendix.

Trianhydrotetrakisdiphenylsilicanediol is the most complex open-chain compound yet isolated, and is formed by carefully hydrolysing tetra-anhydrotetrakisdiphenylsilicanediol.

$$O\begin{<}{Si(C_6H_5)_2.O.Si(C_6H_5)_2 \atop Si(C_6H_5)_2.O.Si(C_6H_5)_2}\end{>}O + H_2O = HO.Si(C_6H_5)_2O.Si(C_6H_5)_2.O.Si(C_6H_5)_2O.Si(C_6H_5)_2.OH$$

This partial hydrolysis is carried out in the following way. The closed chain compound is dissolved in chloroform, and a considerable excess (5 to 6 mols.) of an alcoholic solution of sodium ethoxide is

added. Sufficient chloroform should be present to prevent any precipitation. In not more than a minute slight excess of very dilute acetic acid is added, the whole shaken and the chloroform separated. The aqueous portion is again extracted with this solvent and all the chloroform evaporated at the ordinary temperature. The residue is then treated two or three times with cold ethyl alcohol, which leaves behind a considerable portion of unchanged tetra-anhydrotetrakisdiphenylsilicanediol. The alcoholic extract after filtering is diluted with water and the trianhydrotetrakisdiphenylsilicanediol is obtained after several recrystallisations from a mixture of chloroform and light petroleum. The yield is not good, but further quantities may be obtained by repeating the hydrolysis on the unchanged tetra-derivative.

Trianhydrotetrakisdiphenylsilicanediol crystallises in short, colourless prisms, M.pt. 128·5° C. It resembles the other two open-chain condensation products of diphenylsilicanediol.

Tetra-anhydrotetrakisdiphenylsilicanediol is formed from trianhydrotetrakisdiphenylsilicanediol by warming an alcoholic solution of the latter with a trace of sodium hydroxide. The crystalline precipitate melting at 200° C. when crystallised from ethyl acetate is pure tetra-anhydrotetrakisdiphenylsilicanediol, M.pt. 201° C.

An alcoholic solution of the trianhydrotetrakis-compound with hydrochloric acid does not give so pure a product of the tetra-compound. The tri-body may be converted into the tetra-derivative also by heating the former at 190° to 200° C. for fifteen minutes. Water is evolved, and when decomposition ceases the mass is cooled. Addition of ether causes this to crystallise, and cold alcohol removes only a little soluble matter. The residue on crystallising several times yields pure tetra-anhydrotetrakisdiphenylsilicanediol, which forms well-defined, almost rectangular plates, when deposited from ethyl acetate at the ordinary temperature. These have been measured and the results are recorded in Table XI. of Appendix.

Phenylethylsilicanediol is obtained by hydrolysis of the corresponding disubstituted dichlorosilicanes with aqueous ammonium hydroxide.[1] The diol is deposited in long, transparent needles, when the ethereal solution is evaporated at the ordinary temperature. The compound is recrystallised from ether and light petroleum, and has M.pt. 70° C. It is easily soluble in organic solvents, except light petroleum, in which it is sparingly soluble.

Anhydrobisphenylethylsilicanediol is formed from phenylethylsilicanediol when a pure specimen of the latter is kept in a stoppered bottle at ordinary temperature. The reaction is very slow. An aqueous solution of the diol and a few drops of hydrochloric acid left for twenty-four hours yields a crystalline precipitate of the anhydro-compound. When crystallised from light petroleum and a little ether it forms long, transparent needles, M.pt. 87·5° C.

Dibenzylsilicanediol.[2]—The earlier preparations of the compound are not too satisfactory owing to mixtures being formed, but finally a yield of the diol has been obtained in the following manner:—

Dibenzyl silicon dichloride is melted carefully and dropped into a

[1] Kipping, *Trans. Chem. Soc.*, 1912, 101, 2106.

[2] Dilthey and Eduardoff, *Ber.*, 1905, 38, 4132; Robison and Kipping, *Proc. Chem. Soc.*, 1912, 28, 245; 1913, 29, 348; *Trans. Chem. Soc.*, 1908, 93, 439; 1912, 101, 21; 1914, 105, 40.

5 per cent. solution of potassium hydroxide whilst stirring. The turbid liquid is filtered from the insoluble portion, possibly dibenzyl, then shaken with animal charcoal. When the clear filtrate is made slightly acid with acetic acid a thick, flocculent precipitate is produced. This is difficult to dry, but on leaving several days on a porous plate and finally washing with light petroleum the compound melts at 98° to 100° C., and is almost pure dibenzylsilicanediol. There is a small proportion of substance insoluble in potassium hydroxide present, which seems to point to a slight decomposition after precipitation from the solution of the potassium derivative, due possibly to traces of alkali adsorbed by the somewhat colloidal precipitate. The impurity is not easily eliminated. The method adopted is to dissolve the dibenzylsilicanediol in acetone, then add water until a turbidity is produced, after which the solution is allowed to evaporate spontaneously. The liquid soon shows in addition to milkiness, silky, opaque needles, and these are decanted from the mother-liquors and again dissolved in acetone. This is repeated till the product is completely soluble in 5 per cent. potassium hydroxide.

Dibenzylsilicanediol, M.pt. 101° C., is appreciably soluble in warm water, separating when cold in long, white filaments. If a solution is heated to 90° C. for a short time, decomposition occurs. The presence of hydrochloric acid in a solution causes it to decompose, and a solution in potassium hydroxide when warmed becomes turbid with separation of an oil. When the diol is heated to 100° C. an oily product is formed, which consists essentially of anhydrobisdibenzylsilicanediol, and "termolecular silicone" or trianhydrotrisdibenzylsilicanediol, in small amount. At 130° C. the oil is a mixture of the above two products and other condensation products.

Dibenzylsilicanediol is quantitatively converted into "*termolecular silicone*" when exposed to fumes of hydrogen chloride in a closed vessel. Another convenient means of preparing the silicone is to keep pure dibenzylsilicanediol in alcohol and a little concentrated hydrochloric acid for several days, during which the quantity of crystals increases.

When pure diol is dissolved in a small quantity of acetyl chloride and allowed to evaporate spontaneously, an oil results, which contains unchanged diol and anhydrobisdibenzylsilicanediol. In some instances a good yield of hydrated crystals of the anhydro-body is obtained, using acetyl chloride in ether and light petroleum and evaporating at the ordinary temperature. Hydrated crystals are never formed until the oil containing the anhydrobisdibenzylsilicanediol is exposed to atmospheric moisture or crystallised from solvents containing traces of water.

Anhydrobisdibenzylsilicanediol is formed when 2 mols. of dibenzylsilicanediol condense with loss of 1 mol. of water. Though the yield is not good, the best method of preparation is as follows: Dibenzylsilicanediol (3 grams) is dissolved in 20 c.c. of dry ether, acetyl chloride (30 drops) added, and the solution in a beaker is kept in a desiccator over potassium hydroxide for three hours. It is then connected to the pump and evacuated to remove most of the acid chloride. After six hours, crystals of "termolecular silicone" usually appear on the surface. The solution is then poured into excess of cooled, dilute ammonium hydroxide and shaken. After extraction with ether and evaporation, the oily residue is treated with a little alcohol, which precipitates the silicone. The filtered alcoholic solution is diluted with water, and vigorous rubbing of the beaker with a glass-rod causes

hydrated anhydrobisdibenzylsilicanediol to be deposited. It is purified by dissolving in ether and diluting with light petroleum, then being allowed to evaporate spontaneously after filtration. It is kept in a desiccator over paraffin shavings. The yield is 2 grams of anhydro-compound and 0·9 gram of "termolecular silicone." The former is readily soluble in cold chloroform or benzene, a turbidity occurring due to water of hydration.

Seventy hours' heating of anhydrobisdibenzylsilicanediol at 100° C. gives 6·6 per cent. H_2O ($1H_2O = 3{\cdot}68$ per cent.). When heated at 100° to 110° C. for periods of about ten minutes a stage is reached corresponding with 3·68 per cent. H_2O, after which the loss in weight becomes very small. At 130° to 150° C. the loss is 3·7 per cent. after ten minutes, and then much slower, till in two hours it is 7·8 per cent. This slow loss, after that due to water, is accounted for as being due to volatilisation of benzaldehyde formed by atmospheric oxidation. The odour of the aldehyde becomes more noticeable as the heating is prolonged. Though the remaining oil after heating is probably pure anhydrobisdibenzylsilicanediol, it will not crystallise because it is so hygroscopic. However, the hydrated form is obtainable from the oil by dissolving in light petroleum and allowing the solution to evaporate in air.

Dianhydrotrisdibenzylsilicanediol,

$$HO.Si(CH_2C_6H_5)_2.O.Si(CH_2C_6H_5)_2.O.Si(CH_2C_6H_5)_2.OH$$

is probably present with anhydrobisdibenzylsilicanediol when dibenzylsilicanediol is condensed in the presence of alkalies. If the alkaline solution is heated to 100° C. for some hours the precipitate is partly soluble in cold alcohol, and contains a considerable proportion of trianhydrotrisdibenzylsilicanediol. The dianhydrotris-body is not isolated by the above method, although probably present. Attempts have been made to obtain it by hydrolysis of trianhydrotrisdibenzylsilicanediol which, though practically insoluble in alcohol, slowly dissolves in an alcoholic solution of potassium hydroxide owing to hydrolysis.

DropBooks

$$Si(CH_2.C_6H_5)_2\begin{matrix}O.Si(CH_2C_6H_5)_2\\ O.Si(CH_2C_6H_5)_2\end{matrix}O + H_2O \longrightarrow Si(CH_2C_6H_5)_2\begin{matrix}O.Si(CH_2C_6H_5)_2.OH\\ O.Si(CH_2C_6H_5)_2.OH\end{matrix}$$

Water precipitates a solid which gives with acetic acid dibenzylsilicanediol. Further examination shows it to consist of anhydrobisdibenzylsilicanediol as well as the above diol, or simply the anhydrocompound, or else a compound, M.pt. 82° C., according to the method of procedure. The desired product is that melting at 82° C., and it is obtained in the following manner: A solution of trianhydrotrisdibenzylsilicanediol in cold acetone is treated with 3 per cent. potassium hydroxide (2 mols.) and thirty seconds afterwards a slight excess of dilute acetic acid is added. On further dilution with water an oily precipitate separates, which is filtered and extracted with ether. The solution of the oil in ether is diluted with light petroleum, then left to evaporate. Crystals separate and are recrystallised several times from ether and light petroleum, then dried over sulphuric acid.

Dianhydrotrisdibenzylsilicanediol melts at 82° C. and is readily soluble in all organic solvents except light petroleum, in which it is only sparingly soluble, and insoluble in water or dilute, cold potassium hydroxide. Another method of hydrolysing trianhydrotrisdibenzylsilicanediol is to dissolve it in acetone containing one drop of concentrated hydrochloric acid. After half an hour the solution is diluted with water, vigorously stirred, filtered, and the solid extracted with cold alcohol. In this way the unchanged trianhydrotris-compound is left behind. On dilution of the alcohol with water, an oily substance is obtained which is extracted with ether. The solution contains dianhydrotrisdibenzylsilicanediol, and it is purified by crystallisation from ether and light petroleum. Only 15 per cent. of trianhydro-compound is transferred into dianhydrotrisdibenzylsilicanediol, so further dianhydro-compound is formed by repeating the treatment. It seems probable that the reaction is reversible and equilibrium under the conditions of the equation is when the proportion of dianhydrotris- to trianhydrotrisdibenzylsilicanediol is about 1 to 5, or 1 to 6.

$$H_2O + Si(CH_2C_6H_5)_2\begin{cases}O.Si(CH_2C_6H_5)_2\\ O.Si(CH_2C_6H_5)_2\end{cases}O \rightleftharpoons Si(CH_2C_6H_5)_2\begin{cases}O.Si.(CH_2C_6H_5)_2OH\\ O.Si(CH_2C_6H_5)_2.OH\end{cases}$$

This equation only probably represents one of several reversible reactions, others being :

$$2H_2O + Si(CH_2C_6H_5)_2\begin{cases}O.Si(CH_2C_6H_5)_2OH\\ O.Si(CH_2C_6H_5)_2OH\end{cases} \longleftrightarrow 3Si(CH_2C_6H_5)_2(OH)_2$$

$$2Si(CH_2C_6H_5)_2(OH)_2 \longleftrightarrow OH.Si(CH_2C_6H_5)_2.O.Si(CH_2C_6H_5)_2OH + H_2O$$

Trianhydrotrisdibenzylsilicanediol.—It should be possible to obtain this compound from dianhydrotrisdibenzylsilicanediol, if the reaction mentioned above is reversible. In alcoholic solution the equation should proceed from right to left, as the tri-body is insoluble in alcohol. This actually occurs in the presence of hydrochloric acid, the crystals, M.pt. 98° C., being pure trianhydrotrisdibenzylsilicanediol. The change is complete in twelve hours. This condensation in alcoholic solution goes even more easily with potassium hydroxide than acid, whilst the presence of acetyl chloride has the same effect, though it may be due to the hydrochloric acid formed in this case, and not directly to the acid chloride. The closed-chain compound is not satisfactorily obtained from dianhydrotrisdibenzylsilicanediol by heat.

Trianhydrotrisdibenzylsilicanediol crystallised from chloroform and petroleum-ether mixture has been examined, and the crystallographic measurements are shown in Table XII. of Appendix.

Benzylethylsilicanediol [1] is prepared from pure benzylethyl silicon dichloride, using ice-cold aqueous ammonium hydroxide under the conditions used in the preparation of phenylethylsilicanediol. The ethereal solution is allowed to evaporate spontaneously, when colourless needles

[1] Kipping, *Trans. Chem. Soc.*, 1912, 101, 2106.

are obtained which may be recrystallised from a mixture of ether and light petroleum.

Benzylethylsilicanediol crystallises from hot benzene or boiling light petroleum as transparent needles, but from aqueous acetone or alcohol as cotton-wool-like masses. The compound is appreciably soluble in cold water, more so in hot. It sinters at 80° C., is a pasty mass at 85° C., becoming solid again and more bulky until at 100° C. it melts. Single crystals melt at 85° C. to a clear liquid which becomes turbid if kept at that temperature for a time. Large crystals in a test-tube melt at 98° to 100° C. This suggests that the substance is dimorphous. The change is not due to loss of water, for the compound does not eliminate the elements of water when kept at 85° C. for half an hour. It loses water, however, in a dry vacuum and becomes oily in a day or two. It is thought that the compound contains 1 mol. of water.

Phenylbenzylsilicanediol [1] is most conveniently prepared by dropping the oily dichloride into a 5 per cent. solution of sodium hydroxide. Vigorous stirring is necessary during the reaction. The solution when filtered and treated with slight excess of dilute acetic acid gives a bulky white precipitate of the diol. When filtered and washed it is not quite pure, so it is dissolved in acetone and water added to reprecipitate. This process is repeated until it ceases to give a milky fluid when the water is added, in which case also the compound is completely soluble in alkaline hydroxide. The product is then dried over sulphuric acid. It crystallises in silky needles which melt at 106° C. on rapidly heating, but if kept at 90° C. for a time the compound liquefies and loses the elements of water.

Aryl Derivatives of the Type $(RSiO)_2O$.

DropBooks

Silicobenzoic anhydride [2] is prepared from orthosilicobenzoic ester, $SiC_6H_5(OC_2H_5)_3$, by first converting it into the corresponding acid by aqueous hydrogen iodide, and then dissolving the acid in alcoholic sodium hydroxide and passing in carbon dioxide. The precipitate is washed with absolute alcohol and the solution evaporated. The solid is finally washed with water and dried at 100° C. The anhydride, $(SiC_6H_5O)_2O$, is an amorphous, colourless solid, moderately soluble in ether, less soluble in alcohol, and very slightly soluble in water. It is readily soluble in aqueous potassium hydroxide. Addition of ammonium hydroxide in excess yields silicobenzoic acid, and the anhydride heated with potassium hydroxide furnishes benzene.

Silicotoluic anhydride [3] is prepared from tolyl silicon trichloride by decomposing it with ammonium hydroxide and heating the product at 200° C. The formula corresponds to $(C_7H_7SiO)_2O$, but at a lower temperature it is probably $C_7H_7SiO_2H$, the corresponding acid. It has similar properties to the silicobenzoic anhydride.

Aryl Derivatives of the Type R_2SiO.

Diphenylsilicone, $(C_6H_5)_2SiO$, has not been obtained in a crystalline form.[4]

[1] Kipping, *loc. cit.*
[2] Ladenburg, *Ber.*, 1873, 6, 379.
[3] Ladenburg, *ibid.*, 1874, 7, 387.
[4] Kipping and Lloyd, *Trans. Chem Soc.*, 1901, 79, 449.

Phenylethylsilicone, $(C_6H_5)(C_2H_5)SiO$.[1]—Phenylethylsilicon dichloride, a fuming liquid, can be readily decomposed by water, giving an oil which appears to be the above ketone.

Benzylethylsilicone[2] is produced in the same manner as the preceding compound, from benzylethyldichlorosilicane. It boils at 305° to 315° C. at 22 mm., is not decomposed by the usual reagents, and gives no oxime or hydrazone. The molecular weight in acetic acid solution points to the formula $[(C_6H_5CH_2)(C_2H_5)SiO]_3$.

Aryl Derivatives of the Type $(R_3Si)_2O$.

Diphenylmethylsilicyl oxide is isolated by decomposition of diphenylmethylsilicol at its boiling-point.[3] It forms hexagonal plates, M.pt. 51° to 52° C., is very soluble in the common organic solvents, but sparingly soluble in cold alcohol.

Diphenylethylsilicyl oxide, $[(C_6H_5)_2(C_2H_5)Si]_2O$, M.pt. 65·6° C., is prepared from diphenylethylsilicyl chloride by decomposition with water.[4] The silicol is first formed, and this passes into the corresponding oxide.

Triphenylsilicyl oxide.[5]—When triphenylsilicol is heated with *nitric acid in acetic acid solution it yields small, shining plates of tri*phenylsilicyl oxide, M.pt. 222° C.

Benzylethylbutylsilicyl oxide[6] is formed by the action of water on the corresponding chloride. It is a colourless, viscous liquid, insoluble in water, soluble in alcohol, and boils at 250° to 252° C. The silicol is first formed, but soon passes into the oxide, probably due to traces of impurity, such as hydrochloric acid.

Benzylethylpropylsilicyl oxide[7] is formed in a similar manner to the previous compound. It boils at 256° C.

Sulphobenzylethylpropylsilicyl oxide[8] is prepared by sulphonation of benzylethylpropylsilicyl oxide using sulphuric and chlorosulphonic acids. The body produced is identical with that prepared by sulphonation of *dl*-benzylethylpropylsilicol. This latter compound is isolated by the following series of reactions :—

$$SiCl_4 + MgEtBr = SiEtCl_3 + MgClBr$$
$$SiEtCl_3 + MgPhBr = SiEtPhCl_2 + MgClBr$$
$$SiEtPhCl_2 + MgPrBr = SiEtPhPrCl + MgClBr$$
$$SiEtPhPrCl + MgBzCl = SiEtPhPrBz + MgCl_2 \ (Bz = \text{benzyl})$$
$$SiEtPhPrBz + H_2O(+H_2SO_4) = SiEtPrBzOH + C_6H_6(+H_2SO_4)$$

The silicol formed gives with sulphuric acid a mixture of sulphonic acids, one of which has been isolated as the ammonium salt. It is found

[1] Kipping, *Proc. Chem. Soc.*, 1904, 20, 15.
[2] Kipping, *ibid.*, 1905, 21, 65.
[3] Kipping, *J. Chem. Soc.*, 1927, p. 104.
[4] Marsden and Kipping, *Trans. Chem. Soc.*, 1908, 93, 198.
[5] Kipping and Lloyd, *Trans. Chem. Soc.*, 1901, 79, 449.
[6] Luff and Kipping, *Trans. Chem. Soc.*, 1908, 93, 2004.
[7] Marsden and Kipping, *Trans. Chem. Soc.*, 1908, 93, 198.
[8] Kipping, *Proc. Chem. Soc.*, 1907, 23, 9 ; Marsden and Kipping, *Proc. Chem. Soc.*, 1908, 24, 12 ; Kipping, *Proc. Chem. Soc.*, 1908, 24, 47.

to be a derivative of the corresponding oxide, and possesses the constitution,

$$SO_3H.C_6H_4CH_2.SiEtPr—O—PrEtSi.CH_2C_6H_4.SO_3H$$

It is the externally compensated compound, and though many of its salts with optically active bases crystallise unchanged, the *dextro-methylhydrindamine salt* can be resolved by fractional crystallisation from aqueous methyl alcohol.

The *d*B *d*A-salt is the more sparingly soluble, M.pt. 205° C. The impure *d*B *l*A-salt is from the most soluble fractions, and melts about 135° C.

The *l*B *l*A-salt has been prepared by resolving the acid with *l*-methylhydrindamine.

The two optically active acids have very low specific rotations (roughly, $[\alpha]_D \pm 4°$), but there appears to be ample evidence of their enantiomorphous relationship. Although the acids contain two asymmetric silicon groups, the specific rotations are only $[\alpha]_D \pm 5{\cdot}8°$ to $5{\cdot}9°$ for the sodium salts.

The *d*A *d*B- and *l*A *l*B-methylhydrindamine derivatives vary considerably in outward properties from the *d*A *l*B- and *l*A *d*B-compounds, which have a gelatinous or horny nature, but all four salts have in methyl alcohol solution a specific rotation of $[\alpha]_D \pm 15°$ to 16°.

*d*A *l*B- and *l*A *l*B-menthylamine salts are almost indistinguishable from each other or from the salt of the *dl*-acid. This is also true for the corresponding three *d-bornylamine* compounds. The *cinchonidine* and *cinchonidine hydrogen salts* of the two active acids differ a little in melting-points.

dl-Sulphobenzylethylpropylsilicyl oxide is decomposed by hot concentrated sodium hydroxide, giving paratolnene sulphonic acid.

Sulphobenzylethylisobutylsilicyl oxide [1] can be obtained from any of the following bodies :—

1. *Benzylethylisobutylsilicyl chloride*, $Si.Et(C_7H_7)(C_4H_9)Cl$, B.pt. 198° to 202° C. at 100 mm.

2. *Benzylethylisobutylsilicol*, B.pt. 162° to 164° C. at 25 mm.

3. *Benzylethylisobutylsilicyl oxide*, $[SiEt(C_7H_7)(C_4H_9)]_2O$, B.pt. 250° to 252° C. at 20 mm,

These compounds when sulphonated with chlorosulphonic acid and sulphuric acid each give a mixture, from which the same *dl*-acid, namely, *dl-sulphobenzylethylisobutylsilicyl oxide* is separated as its *l-menthylamine salt*, $[SiEt(C_4H_9)CH_2C_6H_3SO_3H]_2O,2C_{10}H_{21}N.4H_2O$, M.pt. 240° to 245° C., $[\alpha]_D$ −14·7°, in methyl alcohol solution.

dl-Sulphobenzylethylisobutylsilicyl oxide is resolved into its optically active components by fractional crystallisation of its *d-methylhydrindamine salt*. The pure *d*A *d*B-salt melts at 207° to 209° C., and its specific rotation in methyl alcohol solution is $[\alpha]_D$ +16·7°. The specific rotation of the sodium salt of the *d*-acid is $[\alpha]_D$ +10·4°.

The pure *l*A *l*B-salt has M.pt. 207° to 209° C.; $[\alpha]_D$ −17·0° (in methyl alcohol solution) is produced by fractional crystallisation of the salt of the *dl*-acid with *l*-methylhydrindamine. The specific rotation of the sodium salt of the pure *l*-acid is $[\alpha]_D$ −10·5°.

d-Methylhydrindamine *l*-sulphobenzylethylisobutylsilicyl oxide and

[1] Luff and Kipping, *Proc. Chem. Soc.*, 1908, **24**, 224 and 236.

the corresponding *d*A *l*B-salt are prepared by combining the optically pure acids with *d*- and *l*-methylhydrindamine respectively. They are oils at ordinary temperatures.

l-Menthylamine *d*-sulphobenzylethylisobutylsilicyl oxide crystallises well with $4H_2O$. It melts when anhydrous at 254° to 258° C., $[\alpha]_D$ −13·9° (in methyl alcohol solution). The salt of the *l*-acid is very alike in properties, M.pt. 253° to 259° C., $[\alpha]_D$ −17·2°. The salt of the *dl*-acid melts at 240° to 245° C., $[\alpha]_D$ −14·7°.

d-Bornylamine d-sulphobenzylethylisobutylsilicyl oxide melts at 209° to 211° C. The salt of the *l*-acid melts at 210° to 212° C.

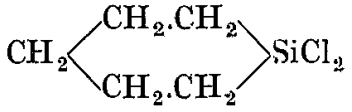
Cinchonidine d-sulphobenzylethylisobutylsilicyl oxide crystallises in needles, M.pt. 171° to 173° C. The salt of the *l-acid* has M.pt. 181° to 183° C. The specific rotations of the two salts are almost alike, the values being $[\alpha]_D$ −68·5° and $[\alpha]_D$ −69·3° respectively in methyl alcohol solution.

The *cinchonidine hydrogen salts* of the *d*- and *l*-acids are crystalline and decompose at 232° to 234° C. and 229° to 231° C. respectively.

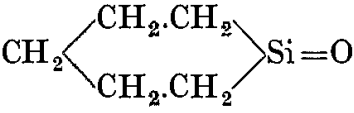
Dibenzylmethylsilicyl oxide [1] is prepared in a similar manner to the previous oxides, by decomposition with water.

Heterocyclic Organo-Silicon Compounds.

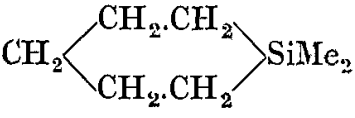
A Polymeride of Cyclopentamethylenesilicone [2] is isolated by the following reactions: Cyclopentamethylenesilicon dichloride is obtained by the action of the organo-magnesium compound derived from 1 : 5 dibromopentane on silicon tetrachloride in ethereal solution. **Cyclopentamethylenesilicon dichloride,**



is a clear, pungent liquid, B.pt. 169·5° to 170·5° C. at 764 mm. (corr.); density 1·1560 at 20° C.; n_D 1·46973 at 20·2° C. This body is hydrolysed by water with production of a yellowish-brown solid, which is possibly a *polymeride* of cyclopentamethylenesilicone,



If instead of silicon tetrachloride, dimethylsilicon dichloride is used, the product of the above reaction is **dimethylcyclopentamethylenesilicane,**



It is a colourless, easily inflammable liquid of slight camphor-like odour, B.pt. 133° to 134° C. at 752·9 mm. (corr.); density 0·8039 at 20° C.; n_D 1·43940 at 20·1° C.[3]

[1] Kipping and Hackford, *Proc. Chem. Soc.*, 1911, 27, 8; *Trans. Chem. Soc.*, 1911, 91, 138.

[2] Bygdén, *Ber.*, 1915, 48, 1236.

[3] An attempt to obtain diethylcyclopentamethylenesilicane gave an impure product, B.pt. 184° to 194° C.

Aryl Derivatives of the Type $RSiO_2H$.

Silicobenzoic acid [1] is isolated from phenyl silicon trichloride by the action of alcohol and subsequently hydriodic acid. *Silicobenzoic acid triethylester* is first obtained, B.pt. 235° C., density 1·0133 at 0° C. and 1·0055 at 10° C. This is completely decomposed by hydriodic acid (B.pt. 127° C.) as follows :—

$$PhSi(OEt)_3 + 3HI = PhSiO_2H + 3EtI + H_2O$$

The compound melts at 92° C. to a viscous liquid, soluble in aqueous alkali, but not reprecipitated at once by dilute hydrochloric acid, though the solution becomes slightly cloudy. If allowed to stand for twenty-four hours, however, the acid completely separates out. If a solution containing excess of potassium hydroxide be evaporated to dryness the potassium salt of the acid is not obtained, but the reaction seems to go as follows :—

$$PhSiO_2K + KOH = C_6H_6 + SiO_3K_2$$

Preparation of pure salts of silicobenzoic acid is not satisfactory. At 100° C. the acid changes to the *anhydride*, $(PhSiO)_2O$—a white, amorphous powder. The anhydride with excess of ammonium hydroxide changes into the acid again, and with potassium hydroxide it yields benzene.[2] Silicobenzoic acid, or phenyl-metasilicic acid as it was called, may also be prepared by the action of dilute ammonium hydroxide on phenyl silicon trichloride. On hydrolysis with water the body possesses the same transparent vitreous properties. Other conditions of preparation give different results. In the course of formation of diphenyl-silicon dichloride from silicon tetrachloride, bromobenzene, and magnesium in the presence of ether, some low fractions consisting of bromobenzene and phenylsilicon trichloride were treated with steam to remove the former compound, and a white, brittle solid was left. To prove its nature pure phenylsilicon trichloride was treated with steam and the white solid repeatedly extracted with ether. The insoluble residue was dried at 120° C., and analysis showed it to be the anhydride of phenyl metasilicic acid. The work of Meads and Kipping seems to point to the possibility that the so-called siliconic acids are merely mixtures (see phenyl silicon trichloride). The composition of various fractions obtained from decomposition of phenylsilicon trichloride with water approximated to $C_6H_5SiO_2H$, but experimental work showed that the so-called *phenylsiliconic acid* was a complex mixture of condensation products of the trihydroxy-compound, $PhSi(OH)_3$.

Tolylsiliconic acid.—There can be little doubt that this and its anhydride are also mixtures.[3]

α-Siliconaphthoic acid, $C_{10}H_7SiO_2H$,[4] is prepared from the corresponding trichloride, $C_{10}H_7SiCl_3$; it melts at 125° to 130° C. to a blistering mass. It is difficultly soluble in aqueous potassium hydroxide, but easily in alcoholic potassium hydroxide.

[1] Friedel and Ladenburg, *Annalen*, 1871, 159, 259; Ladenburg, *Ber.*, 1873, 6, 379.
[2] Kipping and Hackford, *Trans. Chem. Soc.*, 1911, 99, 138; Meads and Kipping, *Trans. Chem. Soc.*, 1914, 105, 679.
[3] Ladenburg, *Ber.*, 1874, 7, 387.
[4] Melzer, *Ber.*, 1908, 41, 3390.

Aryl Derivatives of the Type $R.Si(OEt)_3$.

Silicobenzoic acid triethylester [1] is formed from the trichloride by the action of alcohol.

$$PhSiCl_3+3C_2H_5OH=PhSi(OEt)_3+3HCl.$$

The ester boils at 235° C., and has density 1·0133 at 0° C. and 1·0055 at 10° C.

Ethyl ortho-2 : 4 - dimethylsilicobenzoate, $C_6H_3Me_2Si(OEt)_3$, B.pt. 268° to 271° C., is prepared from ethyl orthosilicate and magnesium m-xylyl iodide.[2]

Benzyl orthosilicic acid triethylester is isolated from benzyl silicon trichloride by treatment with alcohol. It is a colourless oil, B.pt. 170° to 175° C. at 70 mm.[3]

α-Orthosiliconaphthoic acid triethylester, $C_{10}H_7Si(OEt)_3$,[4] is produced in a similar manner to the previous compound. The pure ester boils at 308° to 320° C. at ordinary pressure with partial decomposition, or 174° to 177° C. at 15 to 18 mm.[5]

Aryl Derivatives of the Types, $Si.(OR^1)(OR^2)(OR^3)(OR^4)$; $X.Si(OR^1)(OR^2)(OR^3)$; and $X_2Si(OR^1)(OR^2)$.

These are obtained from silicon tetrachloride as shown by the following equations :—[6]

$$SiCl_4+PhOH \longrightarrow SiCl_3.OPh.+HCl$$
$$SiCl_3OPh+MeOH \longrightarrow SiCl_2OPh.OMe+HCl$$
$$SiCl_2(OPh)(OMe)+EtOH \longrightarrow SiCl(OPh)(OMe)(OEt)+HCl$$

Phenoxymethoxysilicon dichloride is a colourless liquid, B.pt. 216° C. at 752 mm. It readily decomposes with water, giving silicon, hydrochloric acid, methyl alcohol, and phenol. Ethereal ethyl alcohol added to the above compound yields **phenoxymethoxyethoxysilicon chloride**, an oily liquid, B.pt. 241° C.

Methoxyethoxysilicon dichloride is a colourless liquid, B.pt. 128° C. With isobutyl alcohol this body gives *methoxyethoxyisobutoxysilicon chloride,* Si(OMe)(OEt)(OBu)Cl, a liquid, B.pt. 159° to 160° C.

Phenoxymethoxyethoxysilicon chloride cannot be resolved owing to its sensitiveness to moisture. It reacts with the salt of an optically active acid, but decomposes even over sulphuric acid.

Phenoxymethoxyethoxymenthoxysilicon, $Si(OMe)(OEt)(OPh)(OC_{10}H_{19})$, has been prepared only as a thick, colourless oil, which could not be crystallised.

Aryl Derivatives of the Types, $R_3Si-SiR_3$; $R^1R^2R^3Si.SiR^1R^2R^3$.

Hexaphenylsilicoethane.[7]—Five grams of triphenyl silicon chloride in 150 to 200 c.c. of xylene and 2 to 3 grams of metallic sodium are

[1] Friedel and Ladenburg, *Annalen,* 1871, 159, 259.
[2] Khotinsky and Seregenkoff, *Ber.,* 1908, 41, 2946.
[3] Martin and Kipping, *Trans. Chem. Soc.,* 1909, 95, 302.
[4] Melzer, *Ber.,* 1908, 41, 3390; Khotinsky and Seregenkoff, *ibid.,* 1908, 41, 2946; Khotinsky, *ibid.,* 1909, 42, 3088.
[5] Khotinsky and Melzer describe the ester as a thick liquid of aromatic odour, B.pt. 220° to 230° C. at 18 mm.
[6] Kipping and Lloyd, *Trans. Chem. Soc.,* 1901, 79, 449.
[7] Schlenk, Renning, and Racky, *Ber.,* 1911, 44, 1178.

boiled in a dry nitrogen atmosphere with frequent shaking for two hours. The filtrate then deposits thin prisms, with oblique terminal faces of hexaphenylsilicoethane, $Ph_3Si-SiPh_3$, M.pt. 354° C.

dl-Diphenyldiethyldipropylsilicoethane, EtPrPh.Si.Si.EtPrPh.[1]—A freshly prepared specimen of phenylethylpropylsilicon chloride [2] is diluted with an approximately equal volume of dry xylene, then sodium in slight excess of the theoretical amount required is added. When heated to the boiling-point sodium chloride separates; the mixture is well shaken at intervals and intermittent boiling continued for twenty hours. After filtration, the residue is washed with a little xylene and the filtrate distilled at diminished pressure (50 mm.), when the xylene distils over. There are three fractions: 20 per cent. of the whole, B.pt. 165° to 225° C.; 60 per cent., slightly fluorescent, B.pt. 225° to 275° C., and a viscous, yellow, oily residue. Further distillation yields a colourless liquid, B.pt. 265° to 270° C. at 100 mm., this being diphenyldiethyldipropylsilicoethane by analysis and molecular weight determinations. The yield is nearly 50 per cent. This is probably due to the presence of phenylethylsilicon dichloride and phenylethyldipropylsilicane with the required phenylethylpropylsilicon chloride.

Diphenyldiethyldipropylsilicoethane is a rather viscous liquid, with a faint, pleasant, aromatic odour, and its density is less than water. It is only slightly volatile in steam, is slightly soluble in cold methyl alcohol, but easily so when warmed. It is miscible with acetone and most organic solvents. Bromine water reacts with the silicoethane, giving no doubt bromobenzene. Concentrated sulphuric acid at 100° C. causes formation of benzene, in which reaction the compound resembles other silicohydrocarbon derivatives which contain a phenyl group. Unlike other compounds which contain silicon atoms in direct combination, diphenyldiethyldipropylsilicoethane is stable towards hot solutions of alkali hydroxides. This is possibly due partially to the insolubility of the body in aqueous solutions, but even with sodium ethoxide in aqueous acetone there is no appreciable evolution of hydrogen.

dl-Dibenzyldiethyldipropylsilicoethane, EtPr(C_7H_7).Si.SiEtPr(C_7H_7),[3] is obtained from benzylethylpropylsilicyl chloride in a similar manner to the preceding compound. The contents of the flask, however, are boiled only ten hours, and give no reaction for combined halogen. The product seems to be a complex mixture and is distilled at 30 mm., when four fractions are isolated: (1) 30 per cent. of the product, B.pt. 135° to 160° C.; (2) 55 per cent., B.pt. 160° to 240° C.; (3) 10 per cent., B.pt. 240° to 300° C.; (4) 5 per cent., dark brown residue. Refractionation gives a fraction 135° to 160° C. which is mostly dibenzyl, and the principal fraction boils at 240° to 250° C. at 20 mm. This is distilled into two products: (1) 240° to 244° C.; (2) 244° to 248° C. at 20 mm. Both these portions are found by analysis and molecular weight to be almost pure dibenzyldiethyldipropylsilicoethane, but the higher fraction (244° to 248° C.) is the purer sample.

The body is a colourless, moderately mobile liquid, with a faint, pleasant smell, and is specifically lighter than water. It is sparingly soluble in cold methyl alcohol and miscible in most organic solvents. It is practically stable in aqueous alkali hydroxides, and there is no gas

[1] Kipping, *Trans. Chem. Soc.*, 1921, 117, 647.
[2] Kipping, *ibid.*, 1907, 91, 218.
[3] Kipping, *ibid.*

evolution when the compound is warmed in a solution of sodium methoxide in methyl alcohol. It slowly decolorises bromine in carbon tetrachloride solution and fumes are evolved. An acidified solution of potassium dichromate is not appreciably oxidised by the silicoethane.

Sulphonation of dl-dibenzyldiethyldipropylsilicoethane.—A pale yellow emulsion is formed when a quantity of the silicoethane is shaken with concentrated sulphuric acid. On gentle warming the emulsion gives place to a solution which dissolves in cold water. The solution is neutralised with ammonium hydroxide, and when an aqueous solution of brucine hydrochloride is added a colourless precipitate is produced, which gives colourless needles when crystallised from acetone. When, however, a larger quantity of silicoethane is allowed to stand at the ordinary temperature with sulphuric acid, after some hours it changes to a water-clear solution, and this does not all dissolve in a relatively small quantity of water until ammonium hydroxide is added.

Brucine hydrochloride gives a precipitate as before, which is easily soluble in cold acetone, but does not separate in crystals as previously. The brucine salt from the two experiments has been fractionally precipitated from a solution in hot chloroform by addition of benzene. A gelatinous powder results, and this is no longer completely soluble in acetone. The insoluble portion is recrystallised, using the same solvents, and finally a colourless powder is obtained which seems to be the *brucine salt* of the disulphonic acid.[1]

Formula :

$$\left.\begin{matrix}\mathrm{Si.Et.Pr.CH_2.C_6H_4SO_3H}\\ |\\ \mathrm{Si.Et.Pr.CH_2.C_6H_4SO_3H}\end{matrix}\right\}.2\mathrm{C_{23}H_{26}O_4N_2}.2\mathrm{H_2O}$$

l-Menthylamine salt of the disulphonic acid of dibenzyldiethyldipropylsilicoethane.—The brucine salt does not crystallise well, so an aqueous solution of the ammonium salt of the disulphonic acid is treated with an aqueous solution of *l*-menthylamine hydrochloride until there is no more precipitation. The precipitate is filtered and washed with water, then with methyl alcohol. At first a clear liquid comes through the filter, then lustrous crystals separate, but these become pasty as filtration is continued, and addition of water only gives a pasty compound. The crystals cannot be obtained again; possibly they appear owing to a favourable concentration. The pasty menthylamine salt is dried and crystallised from acetone, giving a colourless powder. It is further purified by using a mixture of acetone and methyl alcohol, and finally it is crystallised from wet ethyl acetate. The salt produced is doubtless the *normal l-menthylamine salt* of the disulphonic acid, formula, $\mathrm{C_{24}H_{38}O_6S_2Si_2.2C_{10}H_{21}N.3H_2O}$.[2] Under the microscope the colourless powder appears in fern-like crystals; the anhydrous salt sinters about 208° C., and melts at about 220° C. It is more soluble in wet than dry organic solvents. A solution of the sodium salt of the menthylamine salt seems quite optically inactive; the solution gives precipitates with d-hydrindamine and d-methylhydrindamine hydrochlorides.

[1] An air-dried sample lost 5·1 per cent. of water at 100° C., and the anhydrous salt was hygroscopic.

[2] An air-dried sample lost 6·2 to 6·3 per cent. of water at 100° C.

Aryl Derivatives of the Type Si_4Ph_8 *and* $[SiPh_2]_n$.[1]

When metallic sodium and diphenylsilicon dichloride (rather more of the metal than calculated for the proportion $2Na : SiPh_2Cl_2$) in 3 to 10 volumes of toluene or xylene are heated, reaction occurs as the sodium melts. In some cases the metal was added in small quantities, and in others the dichloride was added slowly to the metal, but either process gives the same result. From the solution, six-sided crystals separate (A), and the solution is cooled and filtered, the dark blue residue being extracted with boiling toluene. This extract deposits crystals of (A), and from the mother-liquors a second crystalline substance (C) is obtained. The dark blue powder, treated with alcohol-acetic acid, then with water, gives a small quantity of flocculent substance (D).

The residue from the original toluene or xylene filtrate is a resinous mass on evaporation, most of it (E) dissolves readily in acetone, leaving a colourless powder from which three crystalline compounds have been obtained: (A) which is only sparingly soluble in boiling toluene, (B) which is readily soluble in cold toluene, and (C) which is even less soluble than (A). These compounds are dealt with below.

"Unsaturated" Silicohydrocarbon, Si_4Ph_8, (A).—This compound crystallises from boiling benzene in short, flat, well-defined prisms, melting about 335° C. It is insoluble in most common solvents at the ordinary temperature, but is appreciably soluble in benzene or toluene, and easily in boiling aniline, benzyl alcohol, or phenol, but prolonged boiling tends to decomposition. It is comparatively stable to boiling aqueous alkalies and sodium methoxide in alcoholic solution, but is rapidly decomposed by boiling with wet piperidine. With iodine in benzene solution it is transformed to octaphenyldi-iodosilicotetrane. When boiled for three to five minutes with tetrachloroethane, a crystalline product is isolated which melts at about 180° C., and is supposed to be the *dichloride*, $Si_4Ph_8Cl_2$. The "unsaturated" silicohydrocarbon is decomposed after five minutes' boiling with nitrobenzene, giving the *oxide* $Si_4Ph_8O_2$ or *diol* $Si_4Ph_8(OH)_2$.

The silico-hydrocarbon also undergoes atmospheric oxidation, is oxidised by boiling with benzaldehyde, ethylene dibromide, bromobenzene, or phosphorus tribromide, or by ozone, when the hydrocarbon is covered with carbon tetrachloride and dilute ozonised oxygen passed in. In all cases the oxide, Si_4Ph_8O, is isolated, and from these reactions Kipping has suggested that this compound may contain tervalent silicon, and be represented by . . . $SiPh_2.SiPh_2.SiPh_2.SiPh_2$ . . .[2]

Octaphenyldi-iodosilicotetrane, $Si_4Ph_8I_2$, prepared from the hydrocarbon as stated above, is a colourless or pale-yellow product, which turns pink and then yellowish-brown on exposure to light and moisture. It crystallises from benzene or ether in lustrous, very acute, rhomboidal plates, which do not melt below 250° C. In cold ether it is only very sparingly soluble, moderately soluble in cold benzene, but these solutions soon turn brown on exposure to air. Hydrolysis of the compound by an ammoniacal solution of acetone yields octaphenylsilicanetetrane oxide, Si_4Ph_8O, and the rhomboidal oxide, $Si_4Ph_8O_2$; the former oxide is also obtained when the hydrolysis is carried out with aniline and water.

[1] Kipping and Sand, *Trans. Chem. Soc.*, 1921, 119, 830, 848.
[2] Kipping, *Trans. Chem. Soc.*, 1923, 123, 2590.

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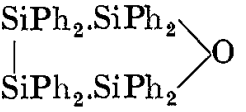
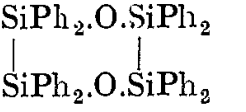
The iodide when treated with sodium in xylene solution gives sodium iodide and the "unsaturated" silicohydrocarbon. With magnesium ethyl bromide, the iodide yields *octaphenyldiethylsilicotetrane*, which crystallises from aqueous acetone containing a little chloroform in flat, transparent, rhomboidal plates, containing 3 mols. of water of crystallisation. When anhydrous, it melts at 253° to 254° C.; when heated with piperidine and sodium hydroxide, it decomposes with evolution of hydrogen.[1]

Octaphenylsilicotetrane oxide,



Formed as just described by the hydrolysis of the di-iodide, it crystallises in microscopic needles, different samples varying in melting-point between 220° and 260° C. It is only slightly soluble in cold alcohol, acetone, glacial acetic acid, ether, or chloroform, but may be crystallised from mixtures of chloroform, benzene, or acetone. From aniline, nitrobenzene, or hot ethyl acetoacetate it crystallises in rosettes of long, transparent prisms, which become opaque when warmed with acetone. Sodium hydroxide in acetone solution attacks it with evolution of hydrogen, and nitric acid or hydrogen bromide in glacial acetic acid solution oxidises it to the rhomboidal oxide.

The Rhomboidal oxide,



crystallises from ethyl acetate, chloroform, or benzene in rhomboidal crystals or in fern-like masses and is apparently dimorphous. It is less soluble in chloroform or benzene than the preceding oxide. It melts sharply to a clear liquid at 221° to 222° C.

Saturated Silicohydrocarbon, Octaphenylcyclosilicotetrane, Si_4Ph_8, (B).—This compound forms short, rectangular prisms, which do not melt at 400° C., but soon become plastic if kept at this temperature. It is very soluble in cold benzene, cold chloroform, or hot ethyl acetate, but sparingly soluble in boiling acetic acid, and almost insoluble in cold acetone, ether, or alcohol. It is very stable towards iodine in benzene solution, bromine, tetrachloroethane, or nitrobenzene, but it is attacked by wet piperidine at 90° C. after several hours. From the decomposition products, diphenylsilicanediol and tetra-anhydrotetrakisdiphenylsilicanediol have been isolated. The former of these two compounds is also obtained from the action of aqueous methyl alcohol or acetone solutions of alkali hydroxides on the silicohydrocarbon. Nitric acid in acetic acid solution partially transforms the silicohydrocarbon to the rhomboidal oxide.[2]

Silicohydrocarbon, $[SiPh_2]_n$, (C), is deposited along with (A) from the toluene extract and requires prolonged extraction to remove it from the blue residue. When the blue salt is treated with alcohol-acetic acid, then with water, (C) and (D) are obtained. These may be separated by

[1] Kipping, *Trans. Chem. Soc.*, 1923, **123**, 2598.

[2] An amorphous form of octaphenylcyclosilicotetrane has recently been prepared (Kipping, *J. Chem. Soc.*, 1927, p. 2727).

prolonged extraction with boiling benzene or toluene. To separate (C) from (A), the latter is converted to the di-iodide, leaving (C) undissolved. The latter crystallises from benzene in lustrous, transparent, six-sided pyramids and rhombohedra. (C), unlike (A), is not affected by boiling tetrachloroethane or nitrobenzene, and it does not react with iodine in boiling toluene or bromine in chloroform solution at ordinary temperature. Prolonged warming with acetic acid containing nitric acid, or with 50 per cent. nitric acid, does not affect it, nor is it acted upon by sodium hydroxide in methyl alcohol or piperidine and sodium hydroxide on heating.[1]

Silicohydrocarbon, $[SiPh_2]_n$, (D).—To isolate (D) the dark blue residue containing sodium and sodium chloride is first extracted with boiling toluene until it appears to be free from (C), then added slowly to alcohol-acetic acid mixture, keeping the acid in excess. After addition of water to the mixture, the insoluble residue is washed with water by a diffusion process, then washed with acetone and extracted with large volumes of hot benzene. It appears to undergo slight atmospheric oxidation, and is more readily oxidised by nitric acid in acetic acid solution than (A), (B), or (C). If the mixture is heated, condensation products of diphenylsilicanediol are principally formed, and a similar result is obtained with an acetic acid solution of potassium permanganate. With nitrobenzene, potassium hydroxide, and piperidine-alkali mixtures, products are obtained which can be converted into diphenylsilicanediol.

When an acetone solution of (E) is kept in a closed vessel it deposits crystals of octaphenylcyclosilicotetrane (B)[2] and a very small proportion of (C). This seems to show that (E) undergoes a transformation into (B). An acetone solution of (E) when treated with alcohol gives at first a white, plastic precipitate, which can be pulled into long threads which change into a very brittle solid as the solvents evaporate. When systematic fractional precipitation is carried out and continued until each of the original fractions has been redissolved and reprecipitated several times, the most sparingly soluble portion, now precipitated in a flocculent form, if again treated with cold acetone, usually gives a very small separation of (B), with traces of (C), and this separation of insoluble matter seems to continue indefinitely. Most of the original preparation, however, is merely resolved into fractions, all miscible with acetone, the more sparingly soluble of which consist of an easily fusible, resinous substance of composition $[SiPh_2]_n$ which may be termed (E_1). When (E) is obtained from diphenylsilicon dichloride of about 95 to 97 per cent. purity, the product after two precipitations consists mainly of (E_1).

The **silicohydrocarbon** (E_1).—When preparations of $[SiPh_2]_n$ are fractionally extracted with boiling alcohol or boiling light petroleum, or precipitated from hot phenol with alcohol, their properties undergo little change, and no crystalline product is isolated save traces of (B). Fractional diffusion of the acetone solution through glazed earthenware also fails to yield crystals. The preparations begin to sinter from 110° to 130° C., but have no definite melting-point. They are miscible with cold ether, benzene, and chloroform, separating out as "glues," which become brittle, but are only sparingly soluble in boiling light petroleum and very sparingly in boiling alcohol or glacial acetic acid. The com-

[1] Kipping, *Trans. Chem. Soc.*, 1924, 125, 2291.
[2] Kipping, *J. Chem. Soc.*, 1927, p. 2719.

pound (E_1) is not particularly reactive with iodine in cold benzene solution, and a little bromine is absorbed in carbon tetrachloride solution, but it takes a long time before the proportion reaches $Br_2 : [SiPh_2]_2$. When (E_1) in partial solution in glacial acetic acid is cautiously oxidised with nitric acid, it yields the rhomboidal oxide, p. 288, but it is almost entirely converted into crystalline and oily condensation products of diphenylsilicanediol.

Action of Sodium on Phenoxydiphenylsilicyl Chloride.

The *phenoxydiphenylsilicyl chloride* required for this reaction is prepared as follows:[1] One mol. of phenol in a little benzene is slowly added to diphenylsilicon dichloride at about 150° C. Hydrogen chloride is evolved and the liquid is heated until no more gas is evolved (about three hours). The product is then distilled at 40 mm., the following fractions being collected: 200° to 240° C. (15 to 20 per cent.); 250° to 260° C. (about 45 per cent.); 280° to 310° C. (large fraction).

Phenoxydiphenylsilicyl chloride, $Si(C_6H_5)_2Cl.OC_6H_5$, is isolated by further fractionation of the portion, B.pt. 250° to 260° C. It is a thick, very faintly fuming oil, B.pt. 252° to 254° C. at 40 mm., miscible with light petroleum, soluble in 5 per cent. potassium hydroxide, yielding the potassium derivatives of phenol and of diphenylsilicanediol. It becomes solid on standing in air, this substance after crystallising from benzene consisting of trianhydrotrisdiphenylsilicanediol.

Diphenoxydiphenylsilicane, $Si(C_6H_5)_2(OC_6H_5)_2$, crystallises from the fraction above 280° C., but it requires fractionating again to obtain a pure product. It crystallises from light petroleum in massive, colourless prisms and octahedra, M.pt. 70° to 71° C., very soluble in ether, chloroform, benzene, or acetone, moderately soluble in cold alcohol.

Freshly distilled phenoxydiphenylsilicyl chloride in 4 volumes of dry toluene is treated with an excess of sodium and heated. The metal becomes covered with a blue crust, and after two to three hours' boiling some colourless crystals are deposited. The hot solution is filtered, the blue residue (I.) washed with toluene, and the combined filtrate and washings evaporated under reduced pressure. The colourless, oily product on treatment with light petroleum yields a crystalline precipitate (II.), and the filtered solution on dilution with more petroleum gives an oily separation (III.). The clear petroleum solution decanted from the oil gives an oily deposit (IV.) when kept at 0° C., but even then contains a large quantity of product (V.).

From the residue (I.) only octaphenylsilicotetrane is isolated.

Diphenoxyoctaphenylsilicotetrane, $PhO.[SiPh_2]_4.OPh$.—The precipitate (II.) consists of octaphenylsilicotetrane and diphenoxyphenylsilicotetrane, the latter being extracted by boiling benzene. When further crystallised from chloroform, then benzene, it separates in well-defined, rhomboidal pyramids and in prisms, M.pt. 215° to 216° C. It is decomposed when heated with piperidine and concentrated sodium hydroxide, giving the sodium derivatives of phenol and diphenylsilicanediol. It is practically insoluble in ether, acetone, alcohol, and glacial acetic acid, but very soluble in boiling aniline.

From fractions (III.) and (IV.) by extraction with light petroleum, diphenoxydiphenylsilicane and some diphenylsilicanediol may be

[1] Kipping, *J. Chem. Soc.*, 1927, p. 2728.

obtained, but the composition of other products has not been definitely settled, and the same applies to the constitution of fraction (V.).

Organometallic Silicon Compounds containing Lead, Tin, and Arsenic.

1 - Triethylsilyl - 4 - trimethylplumbyl-benzene, $Et_3SiC_6H_4PbMe_3$,[1] is obtained from the magnesium compound of triethyl-p-bromophenylmonosilane and trimethyl lead chloride in ether. It is a colourless oil, soluble in absolute alcohol and miscible with ordinary organic solvents. Two atoms of bromine at −75° C. remove the aromatic group, giving $(CH_3)PbBr$ and Et_3-p-$Br.C_6H_4Si$. Triethylsilyl-4-trimethylplumbyl-benzene has a faint smell, boils at 191° C. at 17 mm., and does not decompose on distillation; density 1·4032 at 20° C.; 1·3997 at 23·8° C.; $n_{H\alpha}$ 1·54379, n_D 1·54937, $n_{H\beta}$ 1·56240, $n_{H\gamma}$ 1·57417, at 23·8° C.

1-Triethylsilyl-4-triethylstannyl benzene, $Et_3SiC_6H_4SnEt_3$, is similarly prepared from the magnesium compound of triethyl-p-bromophenyl-monosilane and triethyl tin bromide. It boils at 214° C. at 18 mm.; density 1·1216 at 21·2° C.; $n_{H\alpha}$ 1·52316, n_D 1·52756, $n_{H\beta}$ 1·53888, $n_{H\gamma}$ 1·54864, at 21·2° C.

1-Triethylsilyl-4-diphenylarsyl benzene, $Et_3Si.C_6H_4.AsPh_2$, is produced from the sodium compound of diphenylchloroarsine and triethyl-p-chlorophenyl-monosilane in ether and a little acetic ester. It is a colourless oil, B.pt. 279° to 281° C. at 17 mm.; density 1·1673 at 20° C., 1·1661 at 21·3° C.; $n_{H\alpha}$ 1·60784, n_D 1·61455, $n_{H\beta}$ 1·63181, $n_{H\gamma}$ 1·64718, at 21·3° C.

It is slightly soluble in methyl alcohol and easily in ethyl alcohol and the ordinary organic solvents.

DropBooks

Germanium.

Alkyl Derivatives of Type R_4Ge.

Germanium tetrachloride has been selected as the starting-point for several of these organometallic compounds because it is easily obtainable in a high degree of purity.[2]

Germanium tetramethyl, $Ge(CH_3)_4$.[3]—In 1871 Mendeléeff predicted that germanium or eka-silicon would form volatile organometallic compounds, and it was Winkler, the discoverer of germanium, who in 1886 first produced germanium tetraethyl. Germanium tetramethyl is obtained by the Grignard reaction, and as it is impossible to separate it from ether in the vacuum distillation apparatus,[4] it became necessary to reduce the quantity of ether, which made a specialised apparatus compulsory. Twenty grams of magnesium turnings and 200 c.c. of

[1] Grüttner and Krause, *Ber.*, 1917, 50, 1559.

[2] It was first obtained for this purpose by passing chlorine over crystalline germanium at fairly high temperatures (Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, 44, 304). To avoid the preparation of metallic germanium from the dioxide another method has since been used (Tabern, Orndoff, and Dennis, *J. Amer. Chem. Soc.*, 1925, 47, 2039). Germanium dioxide was suspended in concentrated hydrochloric acid and hydrogen chloride passed into the warm liquid. At 70° C. germanium tetrachloride distilled with traces of hydrochloric acid. By means of a special piece of apparatus all the acid was removed and very pure germanium tetrachloride produced.

[3] Dennis and Hance, *J. Physical Chem.*, 1926, 30, 1055.

[4] Laubengayer and Corey, *J. Physical Chem.*, 1926, 30, 1043.

dry ether are mixed and cooled in ice and salt, and 80 grams of methyl bromide in 100 grams of dry ether at −20° C. are slowly added to the mixture with brisk stirring. When the reaction ceases the contents of the flask are boiled for about half an hour, and then the ether is removed—the last traces by suction. Two hundred c.c. of dry xylene are then introduced. Germanium tetrachloride, 1 mol. to 8 mols. of Grignard reagent, is slowly added to the magnesium methyl bromide, the latter being kept warm. When the reaction ceases the ether is liberated and the xylene kept back by two condensers in the apparatus. The liquid remaining is fractionally distilled, and the greater part passes over at 34° C. Repeated fractionations, however, do not remove the ether from the germanium tetramethyl. Consequently the mixture is treated with about twice its volume of cold concentrated sulphuric acid, and the heavy layer of ethyl sulphuric acid separated from the lighter organometallic compound. This is washed several times, then dried over calcium chloride, and an arc spectrum revealed the product to be practically free from impurity. Germanium tetramethyl is a colourless, oily liquid, of a pleasant, sweet odour, resembling chloroform to some extent, and totally different to germanium tetracthyl. It burns with a sooty flame, which is yellow on the outer surface and deep-red on the inner zone. Nitric acid slowly oxidises it at 0° C., chlorine acts upon it rapidly in the cold, but bromine is much slower in action. Iodine has no effect for forty-eight hours. Germanium tetramethyl is soluble in alcohol, ether, and benzene, and it melts at about −88° C. and boils at 43·4° C. The index of refraction at 23·5° C. is 1·3868, and two density determinations at 0° C. are 1·003 and 1·009.

Germanium tetraethyl.[1]—Winkler first obtained the compound from germanium tetrachloride and zinc diethyl, but the sample was not pure. Dennis and Hance started with pure zinc diethyl, using the reaction of Lachman,[2] heating ethyl iodide with zinc-copper couple at 100° C. They used a series of vessels, so arranged that the zinc diethyl was made, purified, and transferred without contact with the atmosphere. The zinc-copper couple is prepared by heating 25 grams of zinc dust and 200 grams of powdered copper oxide in a current of hydrogen at about 550° to 600° C. till reduction is complete. This is crushed in an agate mortar and mixed with an equal weight of dry sand which has previously been treated with boiling hydrochloric acid. The sand facilitates the penetration of the powder by the ethyl iodide.

The reaction between germanium tetrachloride and zinc diethyl,

$$2Zn(C_2H_5)_2+GeCl_4=2ZnCl_2+Ge(C_2H_5)_4$$

is found to be catalysed by one or both of the products. The zinc chloride does not seem to affect the speed of the reaction, but when germanium tetraethyl is used, although the reaction starts lethargically, it soon becomes so rapid that it is difficult to control. When, however, germanium tetrachloride containing both zinc chloride and germanium tetraethyl is run into zinc diethyl, the reaction continues smoothly to completion. The pasty mixture is freed from zinc diethyl by adding small pieces of ice until the latter is decomposed. A 10 per cent. solution

[1] Winkler, *J. prakt. Chem.*, 1887, 144, 177; Dennis and Hance, *J. Amer. Chem. Soc.*, 1925, 47, 370; Tabern, Orndorff, and Dennis, *ibid.*, 1925, 47, 2039.

[2] Lachmann, *Amer. Chem. J.*, 1900, 24, 36.

of sodium hydroxide is next added and the mixture distilled in steam. Germanium tetraethyl and water are collected. After a second steam-distillation the tetraethyl is separated, dried over calcium chloride, and again distilled.

Germanium tetraethyl has also been obtained by the Grignard reaction. Forty-four grams of ethyl bromide and 9·6 grams of magnesium are converted into ethyl magnesium bromide in the presence of 200 c.c. of ether. To this is added 10·7 grams of germanium tetrachloride in dry benzene. During the addition the liquid is stirred and boiled, and then warmed on a water-bath for three hours. Ice and acetic acid effect the decomposition, the organic solvent layer being separated and the benzene and ether removed by distillation. The residue boils between 155° and 165° C. It is twice treated with concentrated sulphuric acid, washed, dried, then fractionally distilled. The germanium tetraethyl comes over between 162·5° and 163° C. (uncorr.), yield 60 per cent. It is a colourless oil of pleasant, characteristic odour.[1] The compound burns with a flame whose outer part is yellow and inner zone red, shading to blue near the burning liquid. It is slightly soluble in water, and soluble in many organic solvents. It is difficult to oxidise, and chlorine reacts with it but slowly. Germanium tetraethyl boils at 163·5° and melts at −90° C.; density 0·9911 at 24·5° C.; n 1·443 at 17·5° C.

Germanium tetrapropyl, $Ge(C_3H_7)_4$.—It is prepared in the following way: Propyl magnesium bromide is made from 50 grams of propyl bromide, 9·6 grams of magnesium, and 200 c.c. of ether. When the reaction ceases the ether is distilled off and replaced by dry benzene. Eleven grams of germanium tetrachloride in dry benzene are slowly added with constant stirring and boiling. After further boiling for an hour the mixture is decomposed by ice and acetic acid, the solvent layer being separated off, dried, and distilled. The fraction boiling between 200° and 230° C. is shaken with concentrated sulphuric acid, and again washed, dried, and distilled. Most of the oil boils at 225° C., and gives a 76 per cent. yield. It is a colourless, mobile liquid, with a petroleum-like odour. It dissolves in iodine, but at 50° C. it does not react with it to any extent. Ignition of the oil is not easy, but once it begins to burn it liberates a cloud of germanium dioxide; density 0·9539 at 20° C., M.pt. −73° C.; B.pt. 225° C. at 746 mm.;[2] n 1·451 at 17·5° C.

Germanium tetra-n-butyl is a colourless, oily liquid, B.pt. 178° to 180° C. at 733 mm.[3]

Germanium tetra-isoamyl, $Ge(C_5H_{11})_4$.[4]—Sixty-five grams of isoamyl bromide are slowly added to 9·6 grams of magnesium suspended in ether. The ether is replaced by dry benzene and 11 grams of germanium tetrachloride in benzene added, after which the mixture is boiled for three hours. Decomposition is effected in the usual manner and the solvents are eliminated by distillation. The residue is a heavy oil, which decomposes when distilled at ordinary pressure. At 10 mm. it boils mostly at 163° to 164° C. The yield of germanium tetra-isoamyl is 87 per cent.; density 0·9147 at 20° C.; n 1·457 at 17·5° C.

[1] The onion-like odour described by Winkler must have been due to impurities.
[2] Tabern, Orndorff, and Dennis, *J. Amer. Chem. Soc.*, 1925, 47, 2039.
[3] Orndorff, Tabern, and Dennis, *J. Amer. Chem. Soc.*, 1927, 49, 2516.
[4] Tabern, Orndorff, and Dennis, *loc. cit.*

Aryl Compounds of the Type R_4Ge *and their Derivatives.*

Germanium tetraphenyl or **Tetraphenylgermane**, $Ge(C_6H_5)_4$.—This compound may be prepared in several ways, but the most satisfactory method appears to be as follows:[1] The ethereal solution obtained from the interaction of 14·2 grams of magnesium turnings and 76·4 grams of bromobenzene in 200 c.c. of absolute ether is transferred, by means of nitrogen pressure, through a siphon tube into a 3-necked, round-bottomed flask. This flask carries a condenser, a drying tube, a funnel, and a tube reaching to the bottom to permit stirring by a stream of nitrogen. Anhydrous zinc chloride, 33·2 grams, previously dried over phosphorus pentoxide, is suspended in 100 c.c. of ether and slowly added to the Grignard reagent. The mixture is stirred for one hour in the cold, then boiled for one hour, after which 100 c.c. of dry toluene are added and the ether removed on the water-bath. The product is cooled in ice and 14·91 grams of germanium tetrabromide in toluene slowly added with vigorous stirring. The mixture is then boiled for sixteen hours on an oil-bath under an atmosphere of nitrogen. The mass is decomposed by cooling in ice and adding 200 c.c. of 2-Normal sulphuric acid, and the water-toluene mixture then boiled until no solid remains. The toluene layer is separated whilst still warm, dried, and the solvent removed with a vacuum-pump, the residue being recrystallised from benzene and finally washed with low-boiling petroleum. The yield may be as high as 95·4 per cent. if the reaction mixture is boiled sufficiently. The compound has also been obtained: (1) By the interaction of germanium tetrabromide and magnesium phenyl bromide;[2] (2) by the interaction of germanium tetrachloride and magnesium phenyl bromide;[3] (3) by adding germanium tetrachloride to sodium and bromobenzene in ether.

Germanium tetraphenyl is a white, crystalline product, M.pt. 235·7° C., readily soluble in hot benzene, hot toluene, chloroform, moderately soluble in carbon tetrachloride, carbon bisulphide, and acetone, sparingly soluble in alcohol, ether, and petroleum ether. It is not affected by boiling aqueous caustic alkali, or cold concentrated sulphuric acid, but the latter causes sulphonation on warming. Metallic sodium in liquid ammonia reacts slowly with germanium tetraphenyl, yielding sodium triphenyl germanide, $NaGe(C_6H_5)_3$, sodamide, and benzene; and with concentrated sodium solutions the colour changes indicate that a second phenyl group is substituted.[4]

Triphenylgermanium fluoride, $(C_6H_5)_3GeF$, is obtained in practically quantitative yield by heating the corresponding oxide with hydrofluoric acid in a platinum dish. The excess of hydrofluoric acid is evaporated and the product purified by distillation in a vacuum at 150° C. The fluoride melts at 76·6° C. (corr.), is insoluble in water, and only very sparingly soluble in liquid ammonia, but it is extremely soluble in organic solvents. The fluoride is hydrolysed by alkalies, but less readily than the bromide. It reacts with sodium triphenyl germanide to give hexaphenyldigermane. It is the most stable of the triphenyl germanium halides.

[1] Kraus and Foster, *J. Amer. Chem. Soc.*, 1927, 49, 457.
[2] Morgan and Drew, *Trans. Chem. Soc.*, 1925, 127, 1760.
[3] Tabern, Orndorff, and Dennis, *J. Amer. Chem. Soc.*, 1925, 47, 2039.
[4] Kraus and Foster, *loc. cit.*

Triphenylgermanium chloride.[1]—Triphenylgermanium oxide in dry petroleum ether is saturated with hydrogen chloride, when the chloride separates in large, colourless crystals. It may also be obtained by dissolving the oxide in boiling alcohol and adding concentrated hydrochloric acid, or by saturating a solution of triphenylgermanium bromide with hydrogen chloride and cooling. The chloride when crystallised from petroleum ether melts at 117° to 118° C.

Triphenylgermanium bromide was first obtained [2] along with germanium tetraphenyl by the interaction of magnesium phenyl bromide and germanium tetrabromide. It is more readily produced by direct bromination of germanium tetraphenyl in boiling carbon tetrachloride [3] or by brominating in ethylene dibromide, the reaction going to completion after a few minutes' warming in the latter case.[4] It crystallises from petroleum (B.pt. 40° to 80° C.) in large, colourless, transparent, six-sided, refractive, prismatic needles or small compact prisms, M.pt. 138·7° C., very soluble in the usual organic solvents, but sparingly in petroleum ether.

Triphenylgermanium iodide [5] is a very unstable compound, formed by agitating a chloroform solution of the oxide with an aqueous solution of hydriodic acid. It forms pure white crystals from petroleum, M.pt. 157° C. (corr.), but becomes yellow when exposed to air for a few minutes. It readily hydrolyses and its solutions in petroleum ether become pink when exposed to the atmosphere for a short time, owing to the presence of free iodine.

Triphenylgermanium oxide, [6] $Ph_3Ge.O.GePh_3$, is obtained in quantitative yield when an alcoholic solution of triphenylgermanium bromide is boiled with silver nitrate, filtered from silver bromide and diluted with water. It crystallises from hot petroleum (B.pt. 60° to 80° C.) in transparent, colourless prisms, M.pt. 182° to 183° C. In organic solvents it is more soluble than tetraphenylgermane, but less so than triphenylgermanium bromide. Aqueous sodium hydroxide (50 per cent.) does not attack it, but hydrobromic acid (density 1·45) converts it quantitatively into triphenylgermanium bromide.

Sodium triphenyl germanide, $(C_6H_5)_3GeNa$.[7]—Two atoms of sodium react with 1 mol. of hexaphenyldigermane in liquid ammonia according to the equation :

$$2Na + [(C_6H_5)_3Ge]_2 = 2NaGe(C_6H_5)_3$$

The compound is very soluble in liquid ammonia, solutions changing from faint yellow to orange as the concentration increases. Concentrated solutions are extremely viscous, and crystals from liquid ammonia solutions contain 3 mols. of ammonia of crystallisation, which are readily eliminated at low pressures. Sodium triphenyl germanide is also very soluble in benzene saturated with ammonia, and fairly soluble in ether and pure benzene. Solutions in liquid ammonia are as highly ionised as ordinary salts, and benzene solutions in the presence of ammonia readily conduct the current. Sodium triphenyl germanide

[1] Orndorff, Tabern, and Dennis, *J. Amer. Chem. Soc.*, 1927, **49**, 2512.
[2] Morgan and Drew, *loc. cit.*
[3] Kraus and Foster, *loc. cit.*
[4] Orndorff, Tabern, and Dennis, *loc. cit.*
[5] Kraus and Foster, *loc. cit.*
[6] Morgan and Drew, *loc. cit.*
[7] Kraus and Foster, *loc. cit.*

readily oxidises to the germanolate, and with ammonium bromide or water, triphenylgermane is quantitatively produced. The sodium compound with triphenyl germanium fluoride in liquid ammonia gives a small yield of hexaphenyldigermane. Bromobenzene reacts with an ethereal solution of sodium triphenyl germanide, yielding principally germanium tetraphenyl and some hexaphenyldigermane, whilst with tin trimethyl bromide, trimethylstannyl-triphenylgermane is the chief product.

Sodium triphenyl germanolate, $(C_6H_5)_3GeONa$.—This compound is the oxidation product of the preceding derivative, the operation being carried out in the dry state, or in benzene or liquid ammonia solutions. The product obtained from the latter solvent contains 1 mol. of ammonia of crystallisation, and the dry substance does not melt below 250° C. It is very soluble in benzene and petroleum ether, the compound from this solvent melting at about 100° C. The benzene solution is orange in colour.

Triphenylgermane, $(C_6H_5)_3GeH$, is quantitatively prepared by treating sodium triphenylgermanide in liquid ammonia with ammonium bromide or a benzene solution of the same compound with water. The ammonia is evaporated and the germane extracted with petroleum ether, the latter being removed under reduced pressure. The product remaining is distilled in a vacuum at 150° C. at 0·01 mm. pressure. The oily liquid which distils soon becomes a white solid. Triphenylgermane exists in two monotropic forms. The *α-form* is the most stable and melts at 47° C., the *β-form* at 27° C. When the β-form is maintained at 30° C., it completely solidifies immediately when seeded with the α-form. Triphenylgermane is very soluble in most organic solvents and slightly soluble in liquid ammonia. It shows no tendency to decompose up to 250° C.; its hot vapours are irritating and penetrating. On long standing in air it shows signs of oxidation. With halogens or halogen acids it reacts immediately, forming triphenylgermanium halides. Triphenylgermane and sodium in liquid ammonia react to give sodium triphenyl germanide, and coloration of the solution shows the presence of *disodium diphenyl germanide.*

Hexaphenyldigermane,[1] $[(C_6H_5)_3Ge]_2$, occurs when triphenylgermanium bromide in dry xylene is heated with an excess of sodium. The product separates on cooling and is recrystallised from warm benzene. It forms large, transparent cubes which crumble to a powder in the air. It is insoluble in boiling aqueous sodium hydroxide. In ordinary organic solvents it is only slightly soluble, and is practically insoluble in liquid ammonia.[2] When suspended in liquid ammonia and treated with sodium it is slowly converted into sodium triphenyl germanide. Bromination in boiling carbon tetrachloride gives triphenyl germanium bromide.

Trimethylstannyl-triphenylgermane, $(CH_3)_3Sn.Ge(C_6H_5)_3$.—This product is readily obtained by treating a liquid ammonia solution of sodium triphenyl germanide with tin trimethylbromide. It is a white, crystalline solid, M.pt. 88° C., having an odour characteristic of organic tin compounds. It dissolves in most organic solvents and reacts quantitatively with bromine to form triphenyl germanium bromide and tin trimethyl bromide.

[1] Morgan and Drew, *Trans. Chem. Soc.*, 1925, 127, 1760.
[2] Kraus and Foster, *J. Amer. Chem. Soc.*, 1927, 49, 457.

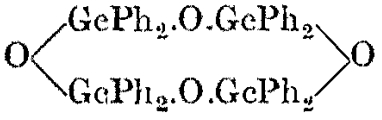
Phenylgermanonic acid (Germanibenzoic acid).[1]—The aqueous mother-liquors from hydrolysis of the Grignard mixture (used in the preparation of germanium tetraphenyl) gradually give a colloidal, white precipitate, which is purified by solution in aqueous sodium hydroxide and reprecipitation by acid. It is a white, amorphous powder.

Triphenyl germanol,[2] $(C_6H_5)_3GeOH$.—Sodium triphenyl germanolate is converted to the germanol by treating its liquid ammonia solution with ammonium bromide or, better still, its benzene solution with water. It melts at 134·2° C. (corr.) and crystallises from petroleum ether in the pure state, but with solvent of crystallisation from benzene.

Tetra-anhydrotetrakisdiphenylgermanediol and **Trianhydrotetrakisdiphenylgermanediol**[3] are both isolated when germanium tetrabromide interacts with 5 mols. of magnesium phenyl bromide. The quantities used are 48·4 grams of bromobenzene (5 mols.), 9·1 grams of magnesium, and 200 c.c. of ether. The resulting Grignard reagent is added to an ice-cold solution of 24·5 grams (1 mol.) of germanium tetrabromide in 100 c.c. of ether. The main product from the ethereal extract is 9 grams of triphenylgermanium bromide (37·5 per cent.). The residual oil, which consists mainly of diphenylgermanium dibromide, together with triphenylgermanium bromide, diphenyl, and bromobenzene, is dissolved in 150 c.c. of alcohol and heated for an hour with 20 grams of silver nitrate in 100 c.c. of alcohol and 40 c.c. of water. The precipitate is mostly silver bromide. The filtrate is evaporated, then steam-distilled to remove diphenyl and o-nitrophenol, and the residue extracted with ether, then cold petroleum. There remains 5 grams of a colourless substance which contains no bromine. It is next dissolved in ethyl acetate several times and fractionally crystallised, when the crystals are hand-picked. Three compounds are separated in this manner: triphenyl germanium oxide, as thin, rhomboidal or pentagonal plates, M.pt. 182° to 183° C.; tetra-anhydrotetrakisdiphenylgermanediol; and trianhydrotetrakisdiphenylgermanediol.

DropBooks

Tetra-anhydrotetrakisdiphenylgermanediol,



forms colourless, cubical, and prismatic crystals, the latter with bevelled and faceted faces. When purified from petroleum or ethyl acetate it melts at 218° C.

Trianhydrotetrakisdiphenylgermanediol, $OH.GePh_2O.GePh_2O.GePh_2O.GePh_2OH$., M.pt. 149° C., forms colourless, hexagonal prisms or flattened, rhomboidal crystals with bevelled edges.[4] Both of these compounds were examined crystallographically by Barker.

Germanium tetra-p-tolyl, $Ge(C_6H_4.CH_3)_4$,[5] is prepared by the Fittig and the Grignard reactions, but the first gives the better result. p-Bromotoluene, 34·2 grams, and 10·7 grams of germanium tetrachloride are dissolved in 300 c.c. of dry ether and 4·8 grams of sodium are gradually added. The residue is extracted with benzene and added

[1] Morgan and Drew, *Trans. Chem. Soc.*, 1925, 127, 1760.
[2] Kraus and Foster, *loc. cit.*
[3] Morgan and Drew, *loc. cit.*
[4] Morgan and Drew, *loc. cit.*
[5] Tabern, Orndorff, and Dennis, *J. Amer. Chem. Soc.*, 1925, 47, 2039.

to the filtrate. Steam-distillation is followed by removal of the solvents, and the pasty mass again dissolved in benzene from which it separates on evaporation, and addition of ether gives germanium tetratolyl as white crystals. Repeated crystallisation from chloroform and benzene yields a pure product, M.pt. 224° C. It is more soluble than the corresponding phenyl compound.

Germanium tetrabenzyl, $Ge(C_6H_5.CH_2)_4$.[1]—Nine grams of magnesium turnings suspended in ether are allowed to react with 5 grams of benzyl chloride. A mixture of 40 grams of benzyl chloride, 10 grams of germanium tetrachloride, and 5 volumes of dry xylene is then added dropwise, with mechanical stirring and gentle refluxing. On conclusion of the reaction, sufficient xylene is added to form a paste, the ether distilled off, and the residue after heating on the steam-bath for some hours is allowed to stand for two days. After working up in the usual manner, and steam-distilling to remove dibenzyl, a nearly quantitative yield of germanium tetrabenzyl is obtained. When pure it melts at 107° to 108° C. and is soluble in alcohol and light petroleum. When slowly dissolved in an excess of 25 per cent. fuming sulphuric acid below 35° C. it yields *germanium tetrabenzyl tetrasulphonic acid.* Its normal *barium salt* dissolves readily and completely in cold water, but is insoluble in acetone, alcohol, and ether.

Germanium triphenyl p-tolyl, $(C_6H_5)_3.Ge.(C_6H_4.CH_3)$, is formed when triphenyl germanium bromide is treated with a large excess of p-tolyl magnesium bromide in ethereal solution. To complete the reaction, the ether is replaced by dry benzene and the whole boiled for eight hours. The reaction product is decomposed by dilute aqueous ammonium chloride and steam-distilled to remove ditolyl. The residue is then crystallised from petroleum ether and alcohol or from glacial acetic acid. The compound melts at 123° to 124° C.

Germanium triphenyl anisyl, $(C_6H_5)_3.Ge.(C_6H_4.OCH_3)$, prepared in a similar manner to the above, melts at 158° to 159° C. It is soluble in alcohol, sparingly soluble in cold glacial acetic acid.

Germanium dimethylanilino triphenyl, $(CH_3)_2NC_6H_4.Ge(C_6H_5)_3$, from triphenyl germanium bromide, p-bromodimethylaniline, and sodium in xylene, forms brownish, crystalline nodules, M.pt. 140° to 141° C. The *hydrochloride* melts with decomposition at 105° to 110° C., is insoluble in water and hydrochloric acid, but soluble in alcohol. When treated with alkali it gives the pure, free base.

Germanium ethyl triphenyl, $C_2H_5.Ge.(C_6H_5)_3$, melts at 75° to 76° C.

Aryl Germanic Acid Anhydrides.

Phenylgermanic acid anhydride, $(C_6H_5GeO)_2O$.—Equimolecular proportions of mercury diphenyl and germanium tetrachloride in dry xylene are heated in a sealed Pyrex bulb for two days, then diluted with dry ether and filtered. The solid residue is pure phenylmercuric chloride, and the filtrate is treated with benzene, and finally with water containing a few drops of ammonium hydroxide. The granular precipitate which separates at the liquid interface is removed and dried at 115° C. The anhydride is a white, fluffy, amorphous solid, with no definite melting-point, soluble in excess of alkali, and reprecipitated by carbon dioxide, insoluble in water and organic solvents.

[1] Orndorff, Tabern, and Dennis, *J. Amer. Chem. Soc.*, 1927, 49, 2512.

p-Tolylgermanic acid anhydride is obtained by a similar process to the above, the reactants being heated at 160° to 190° C., whilst in the case of **benzylgermanic acid anhydride** the temperature required is 115° to 120° C.

Dimethylaminophenylgermanic acid anhydride, $[(CH_3)_2NC_6H_4.GeO]_2O$.—Germanium tetrachloride is heated with an excess of dry dimethylaniline in a sealed flask at 100° to 110° C. for two days. The anhydride is a pearly white, fluffy powder, soluble in very dilute mineral acids and excess of alkali. When kept for some time in an atmosphere of dry hydrogen chloride it is converted into the *hydrochloride* of *dimethylanilino germanium trichloride*:

$$[(CH_3)_2NC_6H_4.GeO]_2O + 8HCl = 2HCl(CH_3)_2NC_6H_4.GeCl_3 + 3H_2O$$

The hydrochloride melts with decomposition at about 110° C.; ammonium hydroxide precipitates the anhydride from its aqueous solution.

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CHAPTER XIII.

ORGANOMETALLIC DERIVATIVES OF TIN.

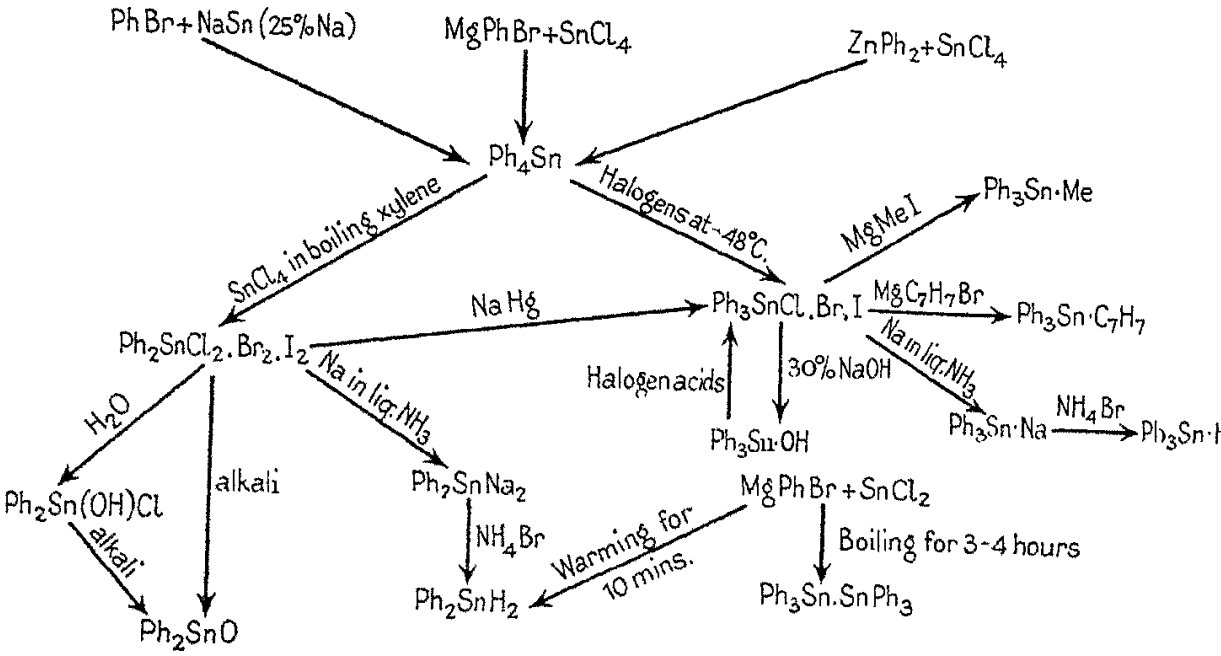
THE first organic compound of tin was prepared by Löwig in 1852. By heating an alloy of 1 part of sodium and 6 parts of tin with ethyl iodide he isolated tin diethyl. In the following year Frankland, by the distillation of this compound, obtained tin tetraethyl. From 1853 onwards the number of organic tin derivatives has steadily increased, and in the last ten years considerable attention has been paid to mixed alkyl compounds of this metal. The type of compound R_4Sn (R=alkyl) comprises only five members, of which most work has been done on the ethyl compound. Following upon its preparation by the above method it was found that tin amalgam containing 14 per cent. of sodium when heated with ethyl iodide would produce tin tetraethyl along with tin triethyl iodide. In 1855 Frankland published his researches on zinc ethyl, and applied this compound to the preparation of tin tetraethyl. The discovery of the Grignard reagents has, however, eradicated all these older methods, and used in combination with stannic chloride or bromide should be capable of producing any tin tetra-alkyl having four like groups attached to the tin. When the type R_4Sn is treated with iodine, one of the alkyl groups is replaced by iodine, and the type R_3SnX produced. This is the starting-point for mixed tetra-alkyls of the type R_3SnR', which may be formed by treating the iodide with zinc alkyls or magnesium alkyl halides. With iodine or bromine at $-40°$ to $-30°$ C. an alkyl group is split out from R_3SnR' and R_3SnX again produced. When the group X in the latter type of compound is iodine, it may be converted to hydroxyl by the action of aqueous alkali. By treatment with suitable acids the hydroxyl group may be replaced by acid radicles. When R_3SnX is heated with sodium at 120° C. the hexa-alkyldistannanes, $R_3Sn.SnR_3$, are formed, and these when acted upon by halogens in the cold, or alkyl iodides at 200° C., revert to R_3SnX. Addition of iodine to the types R_4Sn and R_3SnI gives R_2SnI_2, which reacts with zinc alkyls or magnesium phenyl halides to give R_2SnR_2'. Ammonium or basic hydroxides replace the iodine in R_2SnI_2 by oxygen, and the oxide with hydrogen halides yields the corresponding halides.

A compound of considerable interest is tin trimethyl, which is obtained from tin trimethyl bromide by the action of sodium, the operation being carried out in liquid ammonia.

In 1883 Meyer isolated the first stannonic acid, R.SnO.OH, which gives rise to compounds containing only one alkyl group, $RSnX_3$, when treated with acids. The stannonic acids themselves are prepared by the interaction of alkyl iodides and stannous chloride in potassium hydroxide solution, and are all white, amorphous products.

The reactions of the aromatic compounds of tin are illustrated

generally in the scheme below, the phenyl compounds being used as examples. The heterocyclic derivatives of tin containing the metal in the ring are fully explained in the section dealing with these compounds.



Scheme illustrating the preparation of aromatic tin compounds.

Alkyl Derivatives of the Type R_4Sn.

Tin tetramethyl, $Sn(CH_3)_4$, is isolated by the fractionation of the reaction product formed when 4 parts of tin amalgam (14 per cent. Na) and 3 parts of methyl iodide are heated first on the water-bath and then at 120° C.[1] It is a liquid, the physical constants of which have been given as follows: B.pt. 76° to 78° C.; density 1·338 at 0° C., 1·29136 at 25·5° C.; n_α 1·51749; n_D 1·52009; n_γ 1·53141. The compound is insoluble in water, reduces alcoholic silver nitrate solution, with iodine yields tin trimethyl iodide, and on warming with stannic iodide gives a mixture of tin methyl tri-iodide and tin trimethyl iodide.

Tin tetraethyl[2] may be prepared: (1) By the distillation of tin diethyl. (2) When a tin amalgam containing 14 per cent. of sodium is heated with ethyl iodide, tin tetraethyl is formed, along with some tin triethyl iodide. (3) By adding anhydrous stannous chloride to zinc ethyl, taking care not to use excess of the chloride, and also to keep the temperature down during the reaction. The product is distilled from an oil-bath, and the distillate poured into water, whereby the tin diethyl is destroyed, and the tin tetraethyl obtained as an oil, which is washed, dried, and fractionated.[3] (4) By the interaction of zinc ethyl iodide and powdered tin at 150° to 160° C. Such a high temperature is not required if the tin be added to zinc copper couple and ethyl iodide.

[1] Ladenburg, *Annalen Suppl.*, 1872, 8, 75; Ghira, *Gazzetta*, 1894, **24**, i. 322.

[2] Frankland, *Annalen*, 1853, 85, 340; 1859, **111**, 46; Frankland and Lawrance, *Trans. Chem. Soc.*, 1879, 35, 130; Ladenburg, *Annalen Suppl.*, 1872, 8. 64; Lotts and Collie, *Phil. Mag.*, 1843, [5], **22**, 45: *Jahresber.*, 1886, p. 1601; Pfeiffer and Schnurman, *Ber.*, 1904, 37, 320; Buckton, *Annalen*, 1859, 109, 225; Pope and Peachey, *Proc. Chem. Soc.*, 1903, 19, 290; Gladstone, *Trans. Chem. Soc.*, 1891, 59, 293.

[3] Frankland and Lawrance, *loc. cit.*

Experiments with zinc-tin alloys and ethyl iodide show that in alloys containing from 1 to 50 per cent. of tin, half the latter metal is converted to tin tetraethyl. The yield of this compound is almost proportional to the mass of tin in the alloy, until it contains one-third of its weight of tin, after this the alloy becomes almost inactive, and the time necessary to complete the reaction increases considerably.[1] (5) From tin diethyl di-iodide and zinc ethyl. (6) By the Grignard reaction, using stannic bromide or chloride, yields of 70 and 73 per cent. respectively are obtained. The preparation is carried out as follows: Twenty grams of ethyl bromide and 4·5 grams of magnesium are dissolved in 80 c.c. of dry ether, and then 10 grams of stannic bromide or an equivalent weight of chloride in light petroleum added, and the whole refluxed for one hour. After cooling the mass is decomposed with dilute hydrochloric or acetic acid, the ether layer separated off and dried over calcium chloride. It should be noted that if this ether layer is dried over potassium carbonate, tin triethyl carbonate is formed.

The compound is a mobile, highly refractive liquid, insoluble in water, but soluble in ether. It boils at 175° C.;[2] 180° to 181° C. at 758 mm.;[3] density 1·187 at 23° C.; n_D 1·5143. It is unattacked by aluminium, sodium, or magnesium up to 180° C., but slightly by benzaldehyde. Likewise acetone and ethyl oxalate have no action, nor the following gases at ordinary temperature: ammonia, carbon monoxide, carbon dioxide, cyanogen, nitric oxide, oxygen, or hydrogen sulphide. Sulphur dioxide is slowly absorbed with the formation of tin triethyl-sulphate and tin triethyl ethyl sulphonate. When warmed with concentrated hydrochloric acid, tin tetraethyl yields ethane and tin triethyl chloride; and with thallic chloride, thallium diethyl chloride and tin diethyl dichloride.[4] Treatment with iodine gives ethyl iodide and tin triethyl iodide.

Tin tetrapropyl[5] may be prepared by the interaction of tin tripropyl iodide and zinc dipropyl. It is a liquid, B.pt. 222° to 225° C. at 760 mm. and 116° C. at 13 mm.; density 1·179 at 14° C. and 1·1065 at 20·2° C.; $n_{H\alpha}$ 1·47126, n_D 1·47448, $n_{H\beta}$ 1·48260, $n_{H\gamma}$ 1·48936, at 20·2°.[6]

Tin tetra-isobutyl melts at −13° C. and boils at 143° C. at 16·5 mm., density 1·0540 at 23° C.; $n_{H\alpha}$ 1·47112, n_D 1·47423, $n_{H\beta}$ 1·48206. $n_{H\gamma}$ 1·48863, at 23° C.

Tin tetra-isoamyl[7] is readily prepared by treating isoamyl iodide with tin amalgam, or from magnesium isoamyl chloride and tin tetrachloride.[8] It is a liquid, easily soluble in alcohol or ether and boiling at 188° C. at 24 mm.; density 1·0353 at 19·6° C.; n_α 1·46946, n_D 1·47242, n_β 1·47989, n_γ 1·48607, at 16° C.

Alkyl Derivatives of the Type R_3SnR'.

Tin trimethyl ethyl, $Sn(CH_3)_3(C_2H_5)$, was first isolated from tin trimethyl iodide and zinc ethyl,[9] but later from tin trimethyl iodide and

[1] Letts and Collie, *Proc. Chem. Soc.*, 1886, 2, 166.
[2] Pfeiffer and Schnurmann, *Ber.* 1904, 37, 320.
[3] Frankland, *Annalen*, 1853, 85, 340; 1859, 111, 46.
[4] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 256.
[5] Cahours, *Jahresber.*, 1873, p. 519.
[6] Grüttner and Krause, *Ber.*, 1917, 50, 1802.
[7] Grimm, *Annalen*, 1854, 92, 394.
[8] Krause, *Ber.*, 1918, 51, 1447.
[9] Cahours, *Annalen*, 1862, 122, 48.

magnesium ethyl bromide.[1] The compound is soluble in ether, and boils at 107° to 108° C. under 758 mm.; density 1·243. Treatment with iodine yields ethyl iodide and tin trimethyl iodide.

Tin trimethyl n-propyl is a colourless liquid, boiling at 129° C. at 764 mm.

Tin triethyl methyl has been prepared[2] in the same way as the trimethyl compound. It possesses similar properties to the latter compound, boils at 162° to 163° C., and with iodine splits off the methyl group, yielding tin triethyl iodide.

Tin triethyl n-propyl may be isolated by the action of magnesium n-propyl bromide or iodide on tin trimethyl bromide. It boils at 195° C. at 764 mm.

Table XIII. of the Appendix gives a list of compounds prepared by the following general method, together with their physical constants.[3] Three times the calculated quantity of magnesium alkyl halide is used, and after the introduction of the tin alkyl halides the mixture is boiled under reflux for two hours, the ether removed, and the residue baked on the water-bath for one hour. After cooling, ether is added, and the whole decomposed with water. Mixed tin tetra-alkyls are converted into mixed tin trialkyl bromides of the type $R_2R'SnX$ by the action of bromine at −40° to −30° C., an alkyl group being split out, this resembling the bromination of lead alkyls.

Alkyl Derivative of the Type R_2SnR_2'.

Tin dimethyl diethyl, $Sn(CH_3)_2(C_2H_5)_2$, may be obtained in a variety of ways: (1) From tin diethyl iodide and zinc methyl.[4] (2) From tin dimethyl iodide and zinc ethyl.[5] (3) By the interaction of magnesium methyl iodide and tin diethyl chloride, bromide, or iodide; or by the action of magnesium ethyl bromide on tin dimethyl chloride, bromide, or iodide, the action taking place in ethereal solution.[6]

The compound is a colourless liquid, B.pt. 144° to 146° C.; density 1·2603 at 0° C., or 1·232 at 19° C. It decomposes on distillation, and with iodine the methyl groups are split off and tin diethyl iodide is formed.

For further compounds[7] see Table XIV. of Appendix.

Alkyl Derivatives of the Type $R_2SnR'R''$.

Tin dimethyl ethyl propyl,[8] $Sn(CH_3)_2(C_2H_5).CH_2.CH_2.CH_3$, isolated from the action of magnesium propyl bromide or iodide on tin dimethyl ethyl bromide is a liquid, boiling at 153° C. at 762 mm.

Tin methyl ethyl dipropyl from magnesium propyl bromide and tin methyl ethyl bromide is a colourless liquid, B.pt. 183° to 184° C. at 758 mm.

Tin ethyl n-propyl di-isoamyl[9] boils at 141° to 142° C. at 17 mm.,

[1] Pope and Peachey, *Proc. Chem. Soc.*, 1903, 19, 290.
[2] Cahours, *loc. cit.*
[3] Grüttner and Krause, *Ber.*, 1917, 50, 1802.
[4] Frankland, *Annalen*, 1859, 111, 50.
[5] Morgunow, *Annalen*, 1867, 144, 157.
[6] Pope and Peachey, *loc. cit.*
[7] Grüttner and Krause, *loc. cit.*
[8] Pope and Peachey, *loc. cit.*
[9] Grüttner and Krause, *loc. cit.*

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density 1·0654 at 21·9° C., $n_{H\alpha}$ 1·46902, n_D 1·47214, $n_{H\beta}$ 1·47996, $n_{H\gamma}$ 1·48652, at 21·9° C.

Alkyl Derivatives of the Type R_3SnX.

Tin trimethyl fluoride, $Sn(CH_3)_3F$.[1]—This compound, in common with the other fluorides of tin, may be prepared either by the addition of aqueous hydrofluoric acid to the corresponding trialkyl hydroxide, or by treating alcoholic solutions of other tin trialkyl halides with excess of a neutral aqueous solution of potassium fluoride. The compound forms colourless prisms, which commence to darken at 360° C. and blacken at about 375° C.

Tin trimethyl chloride[2] may be formed from the hydroxide by the action of hydrochloric acid. It has more recently been obtained from tin trimethyl solutions by the action of calcium chloride in dry air, and by treating tin trimethyl with mercuric chloride in ethereal solution.[3] It is a liquid having similar properties to the ethyl compound. It forms a compound with 1 mol. of aniline, and with 1 mol. of pyridine, the latter melting at 37° C.[4] By reduction with sodium in liquid ammonia it yields *sodium trimethyl stannide*, which is a light yellow substance readily decomposing above the temperature of liquid ammonia. It reacts with tin trimethyl halides to give tin trimethyl. The electrical conductivity of tin trimethyl chloride in absolute alcohol at 25° C. has been determined.[5]

Tin trimethyl bromide[6] is formed when tin tetramethyl is treated with bromine.[7] It melts at 27° C. and boils at 165° C.; with ammonia it gives a stable compound, $Me_3SnBr.NH_3$, and with sodium in liquid ammonia, *tin trimethyl* is precipitated. Sunlight acts upon the bromide, forming the compound $(Me_3Sn.OH)_2.Me_3SnBr$, which may also be produced by bringing together the components in benzene solution. In alcoholic solution the complex, $Me_3SnOH.Me_3SnBr.H_2O$, M.pt. 210° to 211° C. with decomposition, is obtained.

Tin trimethyl iodide is obtained in several ways, namely: (1) By heating 4 parts of tin amalgam (14 per cent. Na) with 3 parts of methyl iodide, first on the water-bath, then at 120° C.[8] (2) From 1 part of tin, heated with 2·5 to 3 parts of methyl iodide at 150° to 160° C.[9] (3) By treating tin tetramethyl with iodine. (4) From tin tetra-iodide and magnesium methyl iodide, in ethereal solution.[10] The compound is a liquid, boiling at 170° C. at 760 mm. or 71° C. at 13 mm.; it may be solidified when cooled and melts at 3·4° C. Its density at 0° C. is 2·1432; at 18° C., 2·1096. When dry ammonia is passed into its alcoholic solution, needles separate out, $Me_3SnI.2NH_3$, which are soluble in cold water, but decomposed on boiling, and sparingly soluble in ether.

[1] Krause, *Ber.*, 1918, 51, 1447.
[2] Cahours, *Annalen*, 1860, 114, 354.
[3] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, 47, 2361.
[4] Kraus and Greer, *J. Amer. Chem. Soc.*, 1923, 45, 3078.
[5] Kraus and Callis, *J. Amer. Chem. Soc.*, 1923, 45, 2629; Kraus and Greer, *ibid.*, 1923, 45, 2946.
[6] Cahours, *loc. cit.*
[7] Kraus and Sessions, *loc. cit.*
[8] Ladenburg, *Annalen Suppl.*, 1872, 8, 75; *Ber.*, 1870, 3, 358.
[9] Cahours, *Annalen*, 1860, 114, 367.
[10] Pfeiffer and Heller, *Ber.*, 1904, 37, 4619.

Aniline yields the compound, $Me_3SnI.2PhNH_2$, soluble in alcohol or boiling water, and which may be distilled without decomposition. Crystalline compounds are also obtained with isoamylamine and pyridine, the latter melting at −17° C. The iodide forms the complexes $(Me_3Sn.OH)_2$. Me_3SnI and $Me_3Sn.OH.Me_3SnI.H_2O$, M.pt. 221° C. with decomposition. The electrical conductivity of the iodide in various solvents has been determined.[1]

Tin trimethyl hydroxide is isolated from the iodide by action of potassium hydroxide. It crystallises in prisms and is volatile in steam. The aqueous solution is strongly alkaline, and the solubility in alcohol is greater than in water. With tin trimethyl halides it forms *complexes* of the type $(Me_3SnOH)_2.Me_3SnX$, the *bromide* melting at 113° to 115° C. with decomposition; *iodide* 143° to 153° C. with decomposition; also the type $Me_3SnOH.Me_3SnX.H_2O$, the *chloride*, M.pt. 90° C.; *bromide*, M.pt. 210° to 211° C. with decomposition; *iodide*, M.pt. 221° C. with decomposition. The electrical conductivity of solutions of the hydroxide has been determined by Bredig.[2]

Tin trimethyl sulphate crystallises in brilliant rhombic pyramids, for which $a : b : c = 0{\cdot}8872 : 1 : 1{\cdot}0858$.[3]

Tin trimethyl sulphide, formed by the addition of sulphur to a solution of tin trimethyl in benzene, has M.pt. 6° C., B.pt. 233·5° to 235·5° C. at 759 mm., density 1·649 at 25° C. The corresponding *formate*[4] crystallises in prisms of low melting-point, which can be sublimed, and are easily soluble in water or alcohol. The *acetate* forms needles having similar properties to the formate.

Tin trimethyl ethylate is a liquid boiling at 65° to 66° C., and prepared from the iodide and sodium ethylate at 130° C. It is converted to tin tetramethyl on distillation with sodium.

Tin triethyl salts.—The *fluoride*[5] crystallises from alcohol or acetic acid in large, pure white, glistening prisms, which sublime above 180° C. and melt at 302° C. (corr.), to a colourless, clear liquid. The aqueous solution of the fluoride turns litmus wine-red.

The *chloride* is a liquid of extremely pungent odour, B.pt. 208° to 210° C. or 94° C. at 13 mm.; density 1·428 at 8° C. Cooled to 0° C. it forms a crystalline mass, easily soluble in methyl or ethyl alcohol and ether, sparingly in water.[6] It forms the following double salts, $2Et_3SnCl.PtCl_4$, dark red needles; $Et_3SnCl.PtCl_4$, yellow octahedra.

The *bromide* occurs as a colourless, pungent liquid, B.pt. 222° to 224° C.; density 1·630.[7] It has a similar solubility to the bromide.

The *iodide* may be prepared in a variety of ways: (1) By heating 80 grams of ethyl iodide with 100 grams of tin amalgam (14 per cent. sodium).[8] (2) By the action of iodine on tin tetraethyl. (3) By treating hexa-ethyldistannane with iodine, or heating it with ethyl iodide at about 220° C. It melts at −34·5° C.; B.pt. 231° C. (Ladenburg), 235° to 238° C. (Cahours), 117° C. at 13 mm.,[9] density 1·833 at 22° C. When

[1] Kraus and Callis, *loc. cit.*
[2] Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 303.
[3] Hjortdahl, *Compt. rend.*, 1879, 88, 584; *Jahresber.*, 1879, p. 773; 1880, p. 939.
[4] Cahours, *Annalen*, 1860, 114, 378.
[5] Krause, *Ber.*, 1918, 51, 1447.
[6] Cahours, *Annalen*, 1860, 114. 354.
[7] Löwig, *Annalen*, 1852, 84, 330.
[8] Ladenburg, *loc. cit.*; Löwig, *loc. cit.*, 308; Cahours, *Annalen*, 1860, 114, 246, 361.
[9] Grüttner and Krause, *Ber.*, 1917, 50, 1802.

distilled with potassium hydroxide the base is formed. Heated with sodium the iodide is converted into hexa-ethyldistannane, and by iodine into tin diethyl iodide. The *tin triethyl ethylate* is formed by treatment with sodium ethylate. The following double salts have been prepared: $Et_3SnI.2NH_3$, needles; $Et_3SnI.2C_5H_{13}N$ (isoamylamine) plates.

The *sulphide* is a yellow liquid.[1]

The *hydroxide* is formed from the iodide by the action of aqueous caustic alkali. It crystallises from ether in glistening prisms, M.pt. 43° C. (Ladenburg), 44° to 45° C.,[2] B.pt. 272° C. (Cahours).

The aqueous solution has an alkaline reaction, and prolonged boiling causes the formation of an *anhydride*.

The *sulphate* is dimorphous. The stable form crystallises in hexagonal prisms terminated by pyramids, whose dimensions are very like those of potassium and thallium sulphates.[3]

Tin triethyl sulphate. . .	$a : a\sqrt{3} : c = \cdot5773 : 1 : \cdot7217$.
Potassium sulphate . . .	$a : b : c = \cdot5727 : 1 : \cdot7464$.

The labile form crystallises in regular octahedra. The sulphate is easily soluble in alcohol, sparingly soluble in water.

The *selenate* forms regular octahedra, soluble in water or alcohol.[4] The following salts have also been prepared: *nitrate*, crystalline and easily soluble; *phosphate*, bushy needles, very easily soluble in dilute alcohol, sparingly in ether;[5] *carbonate*, prisms from ether; *cyanide*, needles, which can be sublimed;[6] *cyanate*, prisms; *formate*, needles, subliming when strongly heated, easily soluble in dilute alcohol, sparingly in water; *acetate*, needles, M.pt. 230° C.; *butyrate*, needles; *oxalate*, prisms ($+H_2O$); *tartrate*, cubes; *ditartrate*, crystalline ($+H_2O$); *ethylate*, fuming liquid, B.pt. 190° to 192° C., or 82° C. at 13 mm., density 1·2634 at 0° C., immediately decomposed by water, giving alcohol and tin triethyl hydroxide.

Tin tripropyl salts are as follows: *fluoride*, $(C_3H_7)_3SnF$, crystallises from hot alcohol in prisms, from dilute alcohol in centimetre-long, fine, glistening needles. When heated in a sealed tube it melts at 275° C. to a clear, colourless liquid; the *chloride* has M.pt. −23·5° C., B.pt. 123° C. at 13 mm., and may be obtained from the base; the *bromide* has M.pt. −49° C., B.pt. 133° C. at 13 mm.; the *iodide* has M.pt. −53° C., B.pt. 260° to 262° C., or 141° C. at 13 mm., density 1·692 at 16° C.[7] and is formed in the usual way from n-propyl iodide and tin amalgam. With potassium or ammonium hydroxide it yields the *hydroxide*, which crystallises in prisms. It is volatile and only sparingly soluble in water.

Tin tri-isopropyl salts: the *iodide*,[8] is obtained by the action of tin amalgam (10 per cent. sodium) on isopropyl iodide. It is a liquid, B.pt. 256° to 258° C. With potassium hydroxide it forms the *base*.

Tin tri-isobutyl salts are as follows: *fluoride*, prisms melting at

[1] Kulmiz, *Jahresber.*, 1860, p. 377.
[2] Ladenburg, *Annalen Suppl.*, 1872, 8, 75; *Ber.*, 1870, 3, 358; Cahours, *Annalen*, 1860, 114, 246, 361.
[3] Hjortdahl, *Compt. rend.*, 1879, 88, 584.
[4] Hjortdahl, *Jahresber.*, 1880, p. 939.
[5] Kulmiz, *loc. cit.*
[6] Cahours, *Annalen*, 1862, 122, 50.
[7] Cahours, *Compt. rend.*, 1873, 76, 137; *Jahresber.*, 1873, p. 519.
[8] Cahours, *Compt. rend.*, 1879, 88, 725; Cahours and Demarçay, *ibid.*, 1879, 88, 1112.

244° C. (corr.); *iodide*, B.pt. 284° to 286° C., or 151° C. at 13 mm., density 1·540 at 15° C.;[1] *hydroxide*, B.pt. 311° to 314° C.[2]

The following **tin tri-isoamyl salts** have been isolated: *fluoride*, fine needles, M.pt. 288° C. (corr.); *chloride*, M.pt. 30·2° C., B.pt. 174° C. at 13 mm.; *bromide*, M.pt. 21° C., B.pt. 177° C. at 13 mm.; *iodide*, M.pt. −22° C., B.pt. 302° to 305° C., or 182° C. at 13 mm.; *hydroxide*, B.pt. (without decomposition) 335° to 338° C.

Alkyl Derivatives of the Types $R_2R'SnX$; $RR'SnX_2$; $R_1R_2R_3SnX$.

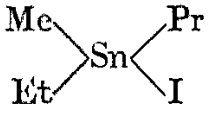
The preparation of the first type of compounds, the tin trialkyl bromides, has already been given under type R_3SnR' (p. 303).[3] The chlorides are formed from the corresponding bromides by dissolving the latter in 5 parts of ether and shaking the solution with half its volume of 33 per cent. alkali. This produces the hydroxide, dilute hydrochloric acid giving the chloride. For list of compounds of type $R_2R'SnX$, see Table XV. of Appendix.

Tin ethyl propyl dichloride.[4]—This compound is obtained from tin ethyl propyl dibenzyl by the action of concentrated sulphuric and chlorosulphonic acid. The aqueous solution of the sulphonation product is treated with ammonium hydroxide, the precipitate filtered off, dissolved in hydrochloric acid, and the acid solution extracted with ether. Removal of the solvent yields the dichloride in needles, M.pt. 57° to 58° C., which have an unpleasant odour, and are readily soluble in alcohol, water, or ether, sparingly in light petroleum.

Tin methyl ethyl n-propyl iodide.[5]—The compound is obtained by the following series of reactions:—

1. $2Me_3SnI + ZnEt_2 = 2Me_3SnEt + ZnI_2$
2. $Me_3SnEt + I_2 = Me_2EtSnI + MeI$
3. $2Me_2EtSnI + ZnPr_2 = 2Me_2EtPrSn + ZnI_2$
4. $Me_2EtPrSn + I_2 = MeEtPrSnI + MeI$

The final product is externally compensated tin methyl ethyl n-propyl iodide,



a faint yellow oil, B.pt. 270° C., practically insoluble in water. When shaken in molecular proportions with an aqueous solution of silver dextro-camphorsulphonate, *tin methyl ethyl n-propyl dextro-camphorsulphonate* is deposited. It crystallises from water in lustrous, square plates, M.pt. 125° to 126° C. In dilute aqueous solution it has a molecular rotation $[M]_D$ +95°, so that for the monobasic radicle Me.Et.Pr.Sn— $[M]_D$ is about 45°. From the mother-liquors of this salt, no salt of the laevo base can be obtained. No better results have been obtained using silver dextro-bromocamphorsulphonate. The *bromocamphor-*

[1] Cahours and Demarçay, *Compt. rend.*, 1879, 88, 1112; Cahours, *ibid.*, 1873, 77, 1404; *Jahresber.*, 1873, p. 520.
[2] Cahours and Demarçay, *Compt. rend.*, 1879, 89, 70.
[3] Grüttner and Krause, *Ber.*, 1917, 50, 1802.
[4] Smith and Kipping, *Trans. Chem. Soc.*, 1912, 101, 2553.
[5] Pope and Peachey, *Proc. Chem. Soc.*, 1912, 28, 42, 116.

sulphonate crystallises from acetone in colourless plates, M.pt. 194° to 197° C., which in dilute aqueous solution have the molecular rotation $[M]_D$ +318°. Allowing the value $[M]_D$ +270° for the bromocamphor-sulphonic acid radicle, this gives $[M]_D$ +48° for the basic radicle, which compares favourably with the previous value.

Alkyl Derivatives of the Type R_2SnX_2.

Tin dimethyl salts.—*Difluoride.*[1]—A solution of 40·3 grams of tin dimethyl di-iodide in 50 c.c. of warm alcohol is treated with a neutral solution of 11·6 grams of potassium fluoride in 25 c.c. of water, when snow-white plates separate out. The fluoride decomposes above 360° C.

The *dichloride* is obtained by treating the oxide with an excess of hydrochloric acid. It crystallises in rhombic prisms, M.pt. 90° C., B.pt. 188° to 190° C., soluble in ether or water, very soluble in alcohol.[2] Measurements of the proportions between the axes gives a : b : c = 0·8341 : 1 : 0·9407.[3] With platinic chloride, $Me_2SnCl_2.PtCl_4,7H_2O$, red rhomboids are produced.

The *dibromide* crystallises in plates from alcohol, M.pt. 74° C.,[4] B.pt. 208° to 210° C.

Di-iodide.—Tinfoil is heated with 2·5–3 parts of methyl iodide at 150° to 160° C. It forms yellow crystals from alcohol-ether solution, M.pt. 30° C., B.pt. 228° C., 33° C. at 13 mm., density 2·872 at 22° C. It is readily soluble in alcohols, ether, or acetone. Its aqueous solution when treated with ammonium hydroxide yields the oxide.

Oxide.—This may be isolated in two ways: (1) It is formed as a by-product, when an alcoholic solution of methyl iodide is shaken for one to two days with alkaline stannous chloride, for details see corresponding ethyl compound.[5] Yield 25 per cent. (2) Heating methyl stannonic acid with concentrated alkali hydroxides.[6] It is an amorphous powder, insoluble in water, alcohol, or ether, and aqueous alkali. With acids it yields the corresponding salts.

Sulphate.—Its crystals consist of rhomboidal prisms, inclined at 74° 50′ with the base and the positive hemiorthodome, the vertical axis making an angle of 83° 75′ with the inclined axis, which is the longest. It is not isomorphous with lead and barium sulphates, although the lengths of its axes are sensibly the same.[7]

Me_2SnSO_4	1·3213 : 1 : 1·6630
$BaSO_4$	1·3127 : 1 : ½(1·6352)
$PbSO_4$	1·2915 : 1 : ½(1·5728)

It is easily soluble in water, but not readily in boiling alcohol.

Diformate.—This is deposited in prisms from alcohol, which partially sublime without decomposition. Its crystals resemble those from calcium, barium, and lead formates.

[1] Krause, *Ber.*, 1918, 51, 1447.
[2] Cahours, *Annalen*, 1860, 114, 374.
[3] Hjortdahl, *Jahresber.*, 1880, p. 390.
[4] Pfeiffer and Lehnardt, *Ber.*, 1903, 36, 3027.
[5] Pfeiffer and Lehnardt, *ibid.*
[6] Pope and Peachey, *Proc. Roy. Soc.*, 1903, 72, 7.
[7] Hjortdahl, *loc. cit.*

Tin dimethyl diformate	.	a : b : c = ·7287 : 1 : ·4784
Calcium formate . . .		,, = ·7599 : 1 : ·4671
Barium formate . . .		,, = ·7650 : 1 : 2(·4319)
Lead formate . . .		,, = ·7417 : 1 : 2(·4219)[1]

A *diacetate*, *dibutyrate*, *divalerate*, and *dicaprylate* have been prepared, also *double salts* of above compounds with pyridine and quinoline.[2]

Tin diethyl salts.—*Difluoride.*—This crystallises in tufts of needles, or rhombic plates, M.pt. 287° to 290° C., previously sintering at 240° C. It forms a double salt, $Et_2SnF_2.2KF$, which crystallises in stout leaflets.

Dichloride.—(1) Prepared by treating the oxide with aqueous chloride solutions, or adding ammonium hydroxide to a hot alcoholic solution of the dichloride—these preparations giving the double salt, $Et_2SnCl_2.Et_2SnO$.[3] (2) By adding hydrochloric acid to the oxide.

The anhydrous compound melts at 84° C., when hydrated at 74° C., B.pt. 220° C., and when freshly prepared it is soluble in alkalies. It forms the following double salts: $Et_2SnCl_2.2NH_3$, an amorphous, white powder, decomposed by water; $Et_2SnCl_2.PtCl_4.7H_2O$, tetragonal bipyramids.

Dibromide.—Occurs as white needles from alcohol, M.pt. 63° C.,[4] B.pt. 232° to 233° C. or 74° C. at 13 mm., easily soluble in water, alcohol, or ether.

Di-iodide.—(1) Obtained by the action of sunlight on a mixture of tin and ethyl iodide or by heating the mixture at 180° C.[5] (2) By heating together tin amalgam and ethyl iodide. (3) From tin tetraethyl and 4 atoms of iodine.[6] (4) From tin triethyl iodide and iodine. (5) From tin diethyl and iodine.[7] It crystallises from alcohol in needles, M.pt. 44° to 45° C.,[8] B.pt. 245° to 246° C., readily soluble in ether or hot water, sparingly in cold water. It forms the following double compounds:—

$$Et_2SnI_2.2NH_3\ ;\ Et_2SnI_2.3Et_2SnO\ ;\ Et_2SnI_2.Et_2SnO$$

The following salts are also known: *sulphate*, crystallises in plates, soluble in alcohol or water; *dinitrate*, crystallises in prisms and forms a double salt with the oxide, $Et_2Sn(NO_3)_2.Et_2SnO.H_2O$; *phosphate*, needles; *diformate*, prisms, easily soluble in water, sparingly in alcohol; *diacetate*, prisms or plates from alcohol, sparingly soluble in water, readily in organic solvents; *dioxalate*, white powder; *di-iodide-dicyanide*, $Et_2SnI_2.Et_2Sn(CN)_2$, a crystalline powder formed from the iodide by the action of silver cyanide; *dithiocyanate*, crystals from alcohol, readily soluble in ether.

Oxide.—(1) Obtained by treating the iodide with ammonium hydroxide. (2) Potassium hydroxide, 23 grams in 150 c.c. of water, is mixed and shaken with 15 grams of stannous chloride in 50 c.c. of water. The black precipitate is filtered off and 10 grams of ethyl iodide added and a fair bulk of alcohol. After six to eight hours' heating on the water-bath, most of the alcohol is distilled off and carbon dioxide passed into the warm

[1] Hjortdahl, *Jahresber.*, 1879, p. 772.
[2] Pfeiffer, *Annalen*, 1910, 376, 310.
[3] Strecker, *Annalen*, 1862, 123, 368.
[4] Werner, *Zeit. anorg. Chem.*, 1898, 17, 90.
[5] Frankland, *Annalen*, 1853, 85, 332; Cahours, *ibid.*, 1860, 114, 354.
[6] Ladenburg, *Ber.*, 1871, 4, 20.
[7] Löwig, *Annalen*, 1852, 84, 321.
[8] Pfeiffer, *Ber.*, 1902, 35, 3303.

solution. Three grams of a white, powdery precipitate are obtained, which consists principally of the required oxide. It is an amorphous powder, insoluble in water, alcohol, or ether, but dissolving readily in acids or alkalies. Hydrogen halides convert it to the corresponding halogen compounds.[1]

Tin dipropyl salts.—*Normal Propyl Compounds: Difluoride.*—This crystallises from methyl alcohol on concentration in rosette-like groups of plates, sintering at 200° C. and melting at 204° to 205° C.

Dichloride.—The di-iodide is dissolved in potassium hydroxide and the solution acidified with hydrochloric acid. It forms magnificent colourless, rhombic crystals, M.pt. 80° to 81° C., consisting of very acute pyramids, with very perfect cleavage parallel to the base, resembling the cleavable pyramids of mercuric bromide.

Tin di-n-propyl dichloride	.	a : b : c = ·6943 : 1 : $\frac{4}{3}$(1·0047)
Mercuric chloride	. .	,, = ·7254 : 1 : 1·0648
Mercuric bromide	. .	,, = ·6817 : 1 : 1·0183 [2]

The *di-iodide* is obtained by heating tin foil with propyl iodide.[3] It boils at 270° to 273° C., but is decomposed on distillation, yielding stannous iodide, and a gas is evolved.

Oxide.—When the preceding compound is treated with potassium or ammonium hydroxides, the oxide separates as a white, amorphous substance. It is insoluble in alcohol, ether, or water. Halogen acids convert it to the corresponding salts.

The following salts are known, most of which appear to have good crystalline structures: *dinitrate, sulphate, diformate, diacetate, oxalate,* and *tartrate.*

Isopropyl Compounds.—The *dichloride,* melting at 56·5° to 57·5° C., insoluble in water, soluble in alcohol or ether, and the *di-iodide,* B.pt. 265° to 268° C., are prepared by the usual methods. *Oxide,* prepared from the trichloride in the usual manner, is an infusible powder. With hot concentrated hydrochloric acid it yields tin di-isopropyl dichloride, transparent crystals from benzene, M.pt. 80° to 84° C., soluble in water, alcohol, hot benzene, or hot glacial acetic acid. With pyridine hydrochloride it gives $(C_3H_7)_2SnCl_2.2C_5H_5N.2HCl$. *Tin di-isopropyl dibromide* forms pale yellow, hygroscopic crystals, melting about 54° C. It also forms a *complex* with pyridine hydrobromide. A *diformate, diacetate,* and *oxalate* are also known.

Tin di-isobutyl salts.—The *dichloride* is a colourless, mobile, heavy liquid, B.pt. 260° to 262° C., solidifying at 5° to 6° C. to a mass of silky needles resembling asbestos, whilst the *di-iodide* occurs as a colourless liquid, B.pt. 290° to 295° C., obtained by heating tin foil and isobutyl iodide to 120° or 125° C. in a sealed tube for several hours. With potassium or ammonium hydroxide it yields a white, amorphous precipitate of the *oxide,* which gives crystalline salts with acids.

Tin di-isoamyl salts.—The following have been isolated: *dichloride,* M.pt. 4° to 5° C.; *sulphate,* white, insoluble powder; *oxide,* amorphous powder,[4]

[1] Pfeiffer, *Ber.,* 1902, 35, 3303.
[2] Hjortdahl, *Jahresber.,* 1879, p. 772.
[3] Cahours and Demarçay, *Compt. rend.,* 1879, 89, 70.
[4] Grimm, *Annalen,* 1854, 92, 384, 390; Cahours and Demarçay, *Compt. rend.,* 1879, 89, 68.

The following ammonia and amine compounds of tin dialkyl halides have recently been described [1]: *tin dimethyl dichloride dianiline*, $Me_2SnCl_2.2PhNH_2$; the *diquinoline* salt forms white crystals, M.pt. 40° to 60° C., unstable in moist air, the *dibromide* melting at 80° to 115° C. Tin diethyl dichloride and dibromide both form *dianiline*, and the latter a *monoaniline* compound. Tin dipropyl dibromide yields a *dianiline* derivative.

All the ammonia compounds are of the type $R_2SnX_2.4NH_3$, except the tin diethyl dichloride compound, which only contains $3NH_3$.

A collection of physical data of various tin alkyls is shown in Table XVI. of the Appendix.[2]

Alkyl Derivatives of the Types R.SnO.OH; $RSnX_3$.

Methyl stannonic acid.[3]—Preparation: Twenty grams of stannous chloride in 50 c.c. of water are added with stirring to 100 c.c. of 20 per cent. potassium hydroxide, and the mixture treated with 14 grams of methyl iodide in 100 c.c. of alcohol. The whole is allowed to stand for three days and should be frequently shaken. The alcohol is removed at 40° C., and hydrochloric acid added until the solution is acid and the white, gelatinous precipitate begins to redissolve. The latter is filtered, washed free from chloride by cold water, and dried *in vacuo* over sulphuric acid. Yield 13·5 grams. The reaction takes place according to the equation:

$$KHSnO_2 + MeI = Me.SnO.OH + KI$$

It may also be obtained from tin methyl tri-iodide by evaporation with an aqueous solution containing 3 mols. of sodium hydroxide.

The acid is a white, amorphous, infusible solid which decomposes at a red heat, leaving stannic oxide. Heated with ammonium nitrate, it yields carbon dioxide, water, and stannic oxide; heated in the absence of air, methane is produced. It is insoluble in water and the usual organic solvents, but readily dissolves in cold solutions of alkali and ammonium hydroxides, or in lime water. It also dissolves in mineral, acetic, and tartaric acids. When ammonium hydroxide is added to the dilute acetic acid solution of the acid, no precipitate is formed until the solution is boiled. This indicates the existence of an ortho acid, $MeSn(OH)_3$, which decomposes on heating to form the stannonic acid. When the acid is boiled with dilute potassium hydroxide a clear solution is never obtained, and if the alkali be concentrated, methane, tin trimethyl hydroxide, and tin dimethyl oxide are formed. Heating with solid potassium hydroxide and a very small quantity of water yields methane and a considerable amount of tin tetramethyl. With concentrated hydriodic acid, the acid yields the iodide, this method being general for the production of the halides. The *complex*, $(MeNHPh)_2.H_2MeSnCl_5$, is prepared by evaporating a solution of the acid and dimethylaniline in dilute hydrochloric acid to the crystallising point. It forms small, white granules, M.pt. 194° C., the aqueous solution having an acid reaction. With aniline a similar *complex* is formed, which crystallises in short prisms, M.pt. 214° C., the clear aqueous solution being

[1] Pfeiffer, *Zeit. anorg. Chem.*, 1924, 133, 91.
[2] Grüttner and Krause, *Ber.*, 1917, 50, 1802.
[3] Meyer, *Ber.*, 1883, 16, 1442; Pfeiffer and Lehnardt, *ibid.*, 1903, 36, 1054; Pope and Peachey, *Proc. Roy. Soc.*, 1903, 72, 7; Druce, *Chem. News*, 1920, 120, 229.

acid to litmus and unchanged on boiling. The pyridine *complex* crystallises in pale yellow plates, M.pt. 300° C.

Tin methyl trichloride, $MeSnCl_3$, is prepared by treating the acid with concentrated hydrochloric acid, phosphorus trichloride, or hydrogen chloride at 100° C. There seems to be a wide difference of opinion regarding the melting-point of the compound: Druce [1] obtained crystals from hydrochloric acid solution, M.pt. 40° C.; Pope and Peachey [2] from light petroleum, long prisms, M.pt. 105° to 107° C., distilling without decomposition at 179° to 180° C.; Pfeiffer and Lehnardt,[3] crystals from ligroin, M.pt. 53° C. It fumes in air and dissolves in water to a clear solution, and is soluble in the usual organic solvents. With aniline it forms the above complex, M.pt. 214° C.

Tin methyl tribromide crystallises in needles or prisms, M.pt. 50° to 55° C. It fumes slightly in air and has a similar solubility to the chloride.

Tin methyl tri-iodide.—Preparation: (1) Methyl stannonic acid is treated with colourless hydriodic acid.[4] (2) Tin tetramethyl (2 parts) and stannic iodide (7 parts) are heated on the water-bath, then allowed to stand for a few hours.[5] (3) Methyl iodide and stannous iodide are heated at 160° C. for four hours.[6] (4) To the solution of 19 grams of methyl iodide and 2·8 grams of magnesium in dry ether, 20 grams of stannic iodide are added in small portions, and the whole boiled for two hours. The mass is decomposed by acidified water and the ether layer separated off and dried. 3·9 grams of oil are obtained between 155° and 180° C., from which 2 grams are isolated between 160° and 170° C. Redistillation gives 1·3 grams of pure iodide, B.pt. 170° C.

The melting-point given by the various investigators varies between 82° and 85° C. The compound crystallises in needles or prisms, very readily soluble in alcohols, ether, ligroin, or chloroform or benzene. Its aqueous solution has a strong acid reaction, nitric acid precipitating iodine. Hot alkali precipitates methyl stannonic acid. Treatment with hydrogen sulphide converts the iodide to the corresponding *sulphide*, which is soluble in ammonium sulphide, but insoluble in the usual organic solvents.

Basic tin methyl sulphate, $MeSn(OH)SO_4.xH_2O$, is obtained as a white powder when methyl stannonic acid is warmed with 50 per cent. sulphuric acid. It slowly dissolves in water, leaving a glassy mass, but cannot be precipitated from its aqueous solution by alcohol.[7]

Ethyl stannonic acid.[8]—Prepared in a similar manner to the methyl compound, it forms a white, amorphous, gelatinous substance which becomes yellowish-brown and transparent on drying. It is insoluble in water and the common organic solvents, but dissolves in dilute mineral acids. When freshly prepared it is soluble in alkali hydroxides, but becomes insoluble after keeping. When strongly heated in the absence of air it yields ethane and ethyl alcohol. The following salts have been prepared: *sodium, potassium, magnesium, barium,* and

[1] Druce, *Chem. News*, 1920, 120, 229.
[2] Pope and Peachey, *Proc. Roy. Soc.*, 1903, 72, 7.
[3] Pfeiffer and Lehnardt, *Ber.*, 1903, 36, 1054.
[4] Pfeiffer and Lehnardt, *loc. cit.*; Pope and Peachey, *loc. cit.*
[5] Pope and Peachey, *Chem. News*, 1903, 87, 253.
[6] Pfeiffer and Heller, *Ber.*, 1904, 37, 4618.
[7] Pfeiffer and Lehnardt, *loc. cit.*
[8] Druce, *Trans. Chem. Soc.*, 1921, 119, 760.

copper; also basic salts of *silver*, *zinc*, *mercury*, *cobalt*, *nickel*, *manganese*, and *strontium*. Solution of the acid in concentrated hydrochloric acid gives a *stannic acid*, $H_2SnEtCl_5$, which forms colourless prisms, decomposed by water, and yields a *potassium* and *aniline* salt. Tin diethyl oxide is formed by boiling the acid with 10 per cent. sodium hydroxide.

Tin ethyl tribromide occurs as colourless, feathery crystals, which become brown on heating, but do not melt at 310° C. It is soluble in water, but the solution soon becomes turbid, owing to the formation of ethyl stannonic acid.

Propyl stannonic acid [1] is obtained by shaking ethyl bromide with an alkaline solution of potassium hydrogen stannite in the presence of alcohol for fourteen days. It is a white powder which yields propane, propyl alcohol, propylene, water, and tin oxides when heated in the absence of air. The acid forms *sodium*, *potassium*, and *basic calcium* and *barium* salts. *Tin propyl tribromide* and *trichloride* are prepared from it in the usual manner, and boiling with 10 per cent. alkali converts them to the dipropyl oxide.

Isopropyl stannonic acid [2] is a white, amorphous substance, giving isopropyl alcohol, propylene, and a trace of propane when heated in the absence of air. It is insoluble in water or organic solvents, but dissolves in dilute mineral acids and alkalies. The *sodium* and *potassium* salts have been obtained, and the oxide is formed in the usual way.

Tin isopropyl tribromide forms deliquescent, pale yellow, prismatic tablets, melting about 112° C. Its aqueous solution is strongly acid. With pyridine hydrobromide it forms the *complex*, $C_3H_7.SnBr_3.2C_5H_5N.2HBr$, which is unchanged at 300° C.

Tin isopropyl trichloride.—This compound has not been isolated in the free state, but only as a *complex* compound with pyridine hydrochloride, analogous to the one from the above bromide.

DropBooks

Alkyl Derivatives of the Types R_2Sn *and* R_3Sn.

Free tin dimethyl,[3] $(Me_2Sn)_x$.—This has been prepared in two ways: (1) A liquid ammonia solution of tin dimethyl dibromide is treated with two atoms of sodium, thus removing the halogen. (2) An ammonia solution of disodium dimethyl stannane is treated with one molecular equivalent of tin dimethyl dibromide. In both cases the group Me_2Sn is precipitated as a yellow solid, insoluble in organic or inorganic solvents and readily oxidising. The substance from preparation (2) is very sensitive to oxygen, even exploding at low pressures.

Tin diethyl [4] has been prepared in a variety of ways: (1) By the action of ethyl iodide on an amalgam containing 1 part of sodium to 6 parts of tin. (2) By reduction of tin diethyl chloride by zinc. (3) The following preparation is due to Pfeiffer: [5] One gram of tin diethyl chloride and 20 grams of 4 per cent. sodium amalgam in ethereal solution are heated for a day on the water-bath in an atmosphere of hydrogen. The product is quickly filtered and dried in a vacuum desiccator.

[1] Druce, *Chem. News*, 1923, 127, 306.
[2] Druce, *Trans. Chem. Soc.*, 1922, 121, 1859.
[3] Kraus and Greer, *J. Amer. Chem. Soc.*, 1925, 47, 2568.
[4] Löwig, *Annalen*, 1852, 84, 309, 313; Frankland, *Annalen*, 1853, 85, 338; Buckton, *Annalen*, 1859, 112, 220.
[5] Pfeiffer, *Ber.*, 1911, 44, 1269.

Pfeiffer claims that tin diethyl may also be prepared by the interaction of ethyl bromide, sodium amalgam, and stannous chloride in an atmosphere of hydrogen. Tin diethyl is obtained as an oil, which gives a clear solution in benzene, ether, or ligroin. When distilled at 25 mm. it forms metallic tin and a brown mass. It instantly reduces silver nitrate to metallic silver. Air oxidises it to tin diethyl oxide, and halogens add on directly forming the corresponding dihalides. Ethyl iodide yields tin triethyl iodide. The density of tin diethyl is 1·558 at 15° C.

Tin trimethyl.[1]—Tin trimethyl bromide is dissolved in liquid ammonia and treated with sodium, when the tin trimethyl is precipitated. It melts at 23° C., and boils at 85° to 88° C. at 45 mm. or 182° C. at 756 mm., and has a density of 1·570 at 25° C. With sodium in liquid ammonia it yields *sodium trimethyl stannide.* It is oxidised in air to an insoluble product, and combines with sulphur in benzene solution to form tin trimethyl sulphide. With halogens, tin trimethyl forms the corresponding halides, the chloride being also formed by the action of calcium or mercuric chloride on ethereal solutions of the compound. Tin trimethyl halides react with sodium trimethyl stannide to form tin trimethyl. The latter, with p-dichlorobenzene and a little ether in liquid ammonia, gives $C_6H_4(SnMe_3)_2$, M.pt. 123° to 124° C., the benzene solution of which gives tin trimethyl iodide and p-di-iodobenzene when treated with iodine, whilst sym-dichloroethane forms tin trimethyl and sodium chloride. Tin triethyl iodide gives $SnMe_3.SnEt_3$, B.pt. 235° C. at 748 mm. Its density at 20° C. is 1·431.

Alkyl Derivatives of the Type $R_3Sn.SnR_3$.

Hexaethyl-distannane.—This compound until 1917 was the only one of its type, and was prepared in the following manner: (1) Tin triethyl iodide heated with sodium.[2] (2) By heating ethyl iodide with 20 per cent. tin amalgam.[3] Molecular weight determinations were carried out by Ladenburg and Rügheimer.[4] It has more recently been prepared[5] by heating 5 grams of sodium powder, 59·2 grams of tin triethyl bromide, and 50 c.c. of dry ether in a sealed tube at about 120° C., with shaking, for ten hours. Yield 90 per cent. The formation of tin tetraethyl and other by-products was not noticed. The compound is a fuming liquid, B.pt. 265° to 270° C.; 146° to 148° C. at 14 mm.; 155° to 157° C. at 19 mm.; density 1·4115 at 0° C. It is insoluble in water and dilute alcohol, and when added to alcoholic silver nitrate, silver is precipitated. Stannic chloride yields tin triethyl chloride, and chlorine tin diethyl chloride. Tin triethyl iodide may be obtained from it, either by the action of iodine or by heating with ethyl iodide at about 220° C. More recently[6] **hexamethyl-distannane** has been obtained in 84 per cent. yield by the interaction of tin trimethyl bromide and metallic sodium in liquid ammonia. By a similar process **trimethyltriethyl-distannane** is obtained as a liquid at ordinary temperatures. The following compounds have been prepared in a similar manner, the

[1] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, 47, 2361.
[2] Ladenburg, *Annalen Suppl.*, 1872, 8, 65.
[3] Cahours, *Annalen*, 1860, 114, 251, 255.
[4] Ladenburg and Rügheimer, *Annalen*, 1909, 364, 51.
[5] Grüttner, *Ber.*, 1917, 50, 1808.
[6] Kraus and Bullard, *J. Amer. Chem. Soc.*, 1926, 48, 2132.

yields being as shown: **hexa-n-propyl-distannane** (88 per cent.), **hexa-isobutyl-distannane** (93 per cent.), **sym. tetraethyl-di-n-propyl-distannane** (88 per cent.), **sym. tetraethyl-di-isobutyl-distannane** (92 per cent.).

The general properties of the compounds may be expressed in the following manner: The hexa-alkyl distannanes are colourless, strongly refracting, and colour-dispersing liquids, only the isobutyl compound (M.pt. 43·8° C.) is solid at the ordinary temperature. They have a penetrating and unpleasant smell, differing distinctly from the tin trialkyl halides. In absolute alcohol they are very slightly soluble, as are the tin tetra-alkyls, but are miscible with organic solvents. In spite of their high boiling-points, they are volatile unchanged under reduced pressure, and on the whole at high temperatures they are just as stable as the tin tetra-alkyls, but in contact with the air they are slowly oxidised to tin trialkyl oxides, in contrast to the tin tetra-alkyls. Treated with halogens in the cold they yield tin trialkyl halides, and also with mercuric chloride or bromide, the latter compounds being reduced to the metal. Anhydrous bismuth bromide splits off an alkyl group. Heated with methyl iodide at 180° C., the stannanes are converted into 1 mol. of tin trialkyl methyl and 1 mol. of tin trialkyl iodide. The grouping ⁝ Sn.Sn ⁝ , besides accounting for the strong optical properties of the compounds, no doubt increases their stability at high temperatures and decreases their stability towards oxidising agents.

Some physical constants of the compounds are shown in Table XVII. of the Appendix.

Disodium tetramethyl-distannane, $NaSnMe_2.SnMe_2Na$.[1]—When metallic sodium is added to tin dimethyl dibromide in liquid ammonia, immediate reaction occurs. If one atom of sodium is added for each atom of bromine in the compound the following reaction takes place:—

$$Me_2SnBr_2 + 2Na = Me_2Sn + 2NaBr$$

The tin dimethyl, which is polymerised, appears as a yellow precipitate. If, however, the addition of sodium is continued, the following change occurs:—

$$2Me_2Sn + 2Na = NaSnMe_2.SnMe_2Na$$

The latter compound gives a red solution in liquid ammonia, and with methyl iodide decomposition occurs in the following manner:—

$$NaMe_2Sn.SnMe_2Na + 2MeI = Me_3Sn.SnMe_3 + 2NaI$$

Disodium dimethyl-stannane, Na_2SnMe_2.—The above compound in liquid ammonia with metallic sodium decomposes according to the equation:

$$NaMe_2Sn.SnMe_2Na + 2Na = 2Na_2SnMe_2$$

This disodium salt gives an intensely red solution in liquid ammonia, which is opaque at high concentrations. With methyl iodide it gives tin tetramethyl,

$$Na_2SnMe_2 + 2MeI = SnMe_4 + 2NaI$$

Disodium hexamethyl-tristannane, $NaSnMe_2.SnMe_2.SnMe_2Na$

[1] Kraus and Greer, *J. Amer. Chem. Soc.*, 1925, 47, 2568.

—This product is formed by the action of tin dimethyl dibromide on a solution of disodium dimethyl stannane. The compound is readily soluble, and chemically very active. With ethyl bromide the two sodium atoms are replaced by ethyl groups, forming $EtSnMe_2.SnMe_2.SnMe_2Et$. This substance is not stable in air, oxidation slowly taking place. It may be distilled under reduced pressures at a temperature of from 80° to 100° C., but some decomposition occurs.

Dodecamethylpentastannane, $Me_3Sn.SnMe_2.SnMe_2.SnMe_2.SnMe_3$, is isolated when disodium hexamethyl tristannane is treated with tin trimethyl bromide.

Dimethylmethylene stannane, $Me_2Sn{=}CH_2$, is prepared by treating disodium dimethyl stannane with methylene chloride. It is a liquid at ordinary temperatures, but oxidises slowly in air and is reactive with halogens. Its properties change with time, pointing to polymerisation taking place.

Aryl Derivatives of the Type R_4Sn.

Tin tetraphenyl, $Sn(C_6H_5)_4$.—This compound has been prepared by three methods: (1) By heating together 500 grams of tin amalgam (25 per cent. Na : 75 per cent. Sn), 600 grams of bromobenzene, and 25 grams of ethyl acetate in an oil-bath.[1] The reaction commences at about 70° C. and is completed by heating the mixture for thirty hours at the boiling-point, a thick brown mass separating out. The latter is boiled with benzene, the solution on cooling giving 100 grams of crude tin tetraphenyl. (2) An easier method of preparation is by use of the Grignard reagent, as follows:[2] To 20 grams of bromobenzene and 3 grams of magnesium dissolved in dry ether, 5 grams of stannic chloride are added drop by drop at room temperature. The mixture is then refluxed for two hours, allowed to stand for a day, decomposed with dilute hydrochloric acid, filtered, and dried. The residue is boiled with pyridine, the cool solution depositing needles of tin tetraphenyl. Yield of pure product, 57 per cent. (3) Zinc diphenyl method.[3] Magnesium phenyl bromide is treated with anhydrous zinc chloride in ether suspension in an atmosphere of nitrogen. After completion of the reaction, toluene is added and the ether distilled off. To the cooled solution, an equivalent amount of stannic chloride in toluene solution is added and the mixture boiled for one hour. The mass is treated with dilute hydrochloric acid and the solution filtered, the residue being extracted with benzene and added to the toluene layer of the filtrate. The mixture is concentrated and cooled, when a 91 per cent. yield of product is obtained, M.pt. 224° to 225° C.

It is easily soluble in hot benzene, pyridine, glacial acetic acid, chloroform, or carbon bisulphide, with difficulty in alcohol or ether, and insoluble in light petroleum. The melting-point is given by various investigators, and ranges between 220° to 226° C. When heated in air, tin oxide results, and the halogens react according to the equation:

$$Sn(C_6H_5)_4 + 2Hal_2 = Sn(C_6H_5)_2Hal_2 + 2C_6H_5Hal$$

[1] Polis, *Ber.*, 1889, *22*, 2915.
[2] Pfeiffer and Schnurmann, *Ber.*, 1904, *37*, 319.
[3] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, *48*, 1054.

When boiled with thallic chloride in xylene solution, the reaction is more complicated, and is best represented as follows :—[1]

(1) $3Sn(C_6H_5)_4+2TlCl_3=2Tl(C_6H_5)_2Cl+2Sn(C_6H_5)_3Cl+Sn(C_6H_5)_2Cl_2$
(2) $Sn(C_6H_5)_2Cl_2+H_2O=Sn(C_6H_5)_2(OH)Cl+HCl$

The following reaction takes place quantitatively with stannic chloride :—[2]

$$Sn(C_6H_5)_4+SnCl_4=2Sn(C_6H_5)_2Cl_2$$

The substance is isomorphous with the tetraphenyls of lead and silicon, and crystallises in prisms belonging to the tetragonal system,

$$a : c=1 : 0{\cdot}3893 ;\ 111 : 110=70° 35'$$

Tin tetra-o-tolyl[3] is prepared by adding 50 grams of stannic chloride in 200 c.c. of ether, drop by drop, to the Grignard solution from 220 grams of o-bromotoluene in 600 c.c. of ether. The whole is boiled for twelve hours under reflux, decomposed with water and ammonium chloride, the ethereal solution being separated off. The product remaining in suspension is recovered by washing the residue with alcohol, and refluxing it with benzene. The crude product is steam-distilled, to remove o-bromotoluene and di-o-tolyl, and recrystallised from 400 c.c. of ether. Yield 35 per cent. The product consists of a snow-white powder, fairly soluble in benzene, less so in ether, and insoluble in alcohol. It crystallises from ether in tufts of very fine needles, M.pt. 158° to 159° C.

Tin tetra-m-tolyl.[4]—The preparation is similar to the preceding one, but the yield is only 29 per cent. It crystallises in colourless, glistening needles from absolute alcohol, M.pt. 128·5° C., easily soluble in cold benzene, boiling ether, or boiling alcohol, with difficulty in cold ether or alcohol.

Tin tetra-m-xylyl, $(Me_2C_6H_3)_4Sn$, is obtained by treating the Grignard solution from 329 grams of 1-bromo-2 : 4-xylene in 800 c.c. of ether, with 80 grams of stannic chloride. The yield is only 15 grams or 7·2 per cent. It crystallises from benzene on the addition of ether in doubly refracting needles, a millimetre long, M.pt. 224° C. (corr.). Heated in a sealed tube, the molten substance becomes yellow at 287° C., and decomposes about 360° C.

Tin tetra-p-xylyl crystallises from benzene in quadratic columns or cubes, M.pt. 278° C. (corr.), becoming yellow at 342° C., darker at 347° C., and decomposing at 360° C. Yield 50 per cent.

Tin tetra-cyclohexyl.[5]—Cyclohexyl bromide, 192 c.c. (250 grams), or 182 c.c. (182 grams) of cyclohexyl chloride, are converted into the magnesium compound, the mixture being heated for two hours to complete the reaction. The ethereal solution is then poured off and mixed with 300 c.c. of pure, dry benzene. To the mixture, with ice cooling and mechanical stirring, 75 grams of stannic chloride in 200 c.c. of dry benzene are slowly added dropwise. The reaction is violent and completed by three hours' boiling. The mass is decomposed by ice-

[1] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, **121**, 256.
[2] Goddard, Ashley, and Evans, *Trans. Chem. Soc.*, 1922, **121**, 978.
[3] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2150.
[4] Krause and R. Becker, *Ber.*, 1920, 53, [B], 184.
[5] Grüttner, *Ber.*, 1914, 47, 3257 ; Krause and Pohland, *ibid.*, 1924, 57, [B], 535.

DropBooks

water and treated with 5 per cent. hydrochloric acid to dissolve the basic magnesium salts. The benzene-ether layer is separated, washed, dried, and evaporated to about 35 c.c. bulk. Crystals separate on cooling, and are recrystallised from benzene by the addition of alcohol. This crude product is changed to the monobromide, and the latter treated with cyclohexyl magnesium bromide, when pure tin tetra-cyclohexyl is obtained. It crystallises from benzene in small, colourless, quadratic plates, resembling the corresponding lead compound. The pure compound sinters at 263° to 264° C., at 290° C. a yellowish cloudiness appears, and at 307° C. the product suddenly becomes dark gray and tin separates out. When pure it is odourless, air-stable, very soluble in hot benzene, moderately soluble in warm ether, and sparingly in hot alcohol. By the action of bromine in carbon disulphide solution, tin di-cyclohexyl dibromide is formed, and iodine gives the corresponding di-iodide, but stannic chloride only removes one cyclohexyl group, giving tin tri-cyclohexyl chloride.

Tin tetrabenzyl[1] is obtained by treating 1 mol. of stannic chloride in ether, in the presence of 4 atoms of magnesium, with an ethereal solution of 4 mols. of benzyl chloride. After completion of the reaction the ether is distilled off, and the residue heated at 100° C. for two to three hours. On cooling, the mixture is decomposed by water, steam-distilled, and filtered, the dry residue being crystallised from light petroleum. The compound forms colourless, well-defined prisms, M.pt. 42° to 43° C., which are readily soluble in most organic solvents. It is oxidised in the atmosphere at ordinary temperatures, forming benzaldehyde, this often being noticed with benzyl compounds of tin.

Tin tetra-α-thienyl,[2] $(C_4H_3S)_4Sn$.—A suspension of stannic chloride in ether is slowly added to the Grignard solution from α-iodothiophene and magnesium in dry ether, and the reaction is completed by boiling for one hour on the water-bath. On working up in the usual manner, tin tetra-2-thienyl is obtained in needles or prisms, M.pt. 156° C. (corr.), fairly soluble in benzene, hot ether, and hot alcohol, sparingly soluble in cold ether, and insoluble in cold alcohol. The alcoholic solution when boiled with silver nitrate remains unchanged.

Aryl Derivatives of the Types Ar_3SnAr' *and* Ar_3SnAlk.

The compounds are prepared in a similar manner to the corresponding derivatives of lead, the starting-point being tin triphenyl chloride, but the yields in this case are practically quantitative.[3]

Tin-triphenyl p-tolyl crystallises from ether in fine rosettes of needles, M.pt. 124° C., and from hot alcohol in tufts resembling glass wool. It is also soluble in benzene and chloroform.

Tin triphenyl p-xylyl crystallises from hot alcohol in colourless, oblong, hexagonal plates, M.pt. 100·5° C. The solubility of the body is similar to that of the above tolyl compound.

Tin triphenyl α-naphthyl crystallises from alcohol in colourless, refractive prisms, M.pt. 125° C.

Tin triphenyl cyclohexyl is obtained from tin triphenyl chloride and an excess of magnesium cyclohexyl bromide. It forms bushy, colourless

[1] Smith and Kipping, *Trans. Chem. Soc.*, 1912, 101, 2553.
[2] Krause and Renwanz, *Ber.*, 1927, 60, [B], 1582.
[3] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2150.

needles, M.pt. 131° to 132° C., easily soluble in benzene or ether, sparingly in alcohol. An iodine solution in benzene shows very little reaction in the cold, but at 60° to 70° C. slowly produces a pale yellow oil which crystallises from alcohol in plates, M.pt. 45° C., and no tin triphenyl iodide is produced.

Tin tricyclohexyl phenyl is obtained from tin tricyclohexyl bromide, and recrystallised from benzene-alcohol mixture. It crystallises in snow-white, microscopic, fern-like ramifications of crystals, M.pt. 191° to 192° C., easily soluble in benzene or chloroform, sparingly in hot alcohol, and insoluble in cold.

Tin tricyclohexyl p-tolyl, melting at 111° C., is a pure white, granular powder, crystallising from hot alcohol in prismatic rods.

Tin triphenyl methyl [1] crystallises from ethereal solution on concentration in colourless tetrahedra, melting at 60° C. to a clear, colourless liquid. From this melt it crystallises in large, glittering rhomboids, readily soluble in benzene, chloroform, or ether, sparingly in cold 95 per cent. alcohol. Its density at 63·85° C. is 1·3113; n_{H_α} 1·60001, n_D 1·60661, n_{H_β} 1·62351, n_{H_γ} 1·63831, at 63·85° C. From these data the following are calculated :—

$$\Sigma R_{H\alpha}\ 26{\cdot}09,\ \Sigma R_D\ 26{\cdot}32,\ \Sigma\Delta_{\gamma-\alpha}\ 1{\cdot}328,\ \Sigma\Delta_{\beta-\alpha}\ 0{\cdot}819$$
$$MR_{H\alpha}\ 95{\cdot}21,\ MR_D\ 96{\cdot}06,\ M\Delta_{\gamma-\alpha}\ 4{\cdot}85,\ M\Delta_{\beta-\alpha}\ 2{\cdot}990$$

Subtracting the value of the atomic refractions of carbon and hydrogen, the following values are obtained for the atomic refraction and atomic dispersion of tin in the compound :—

$$AR_{H\alpha}\ 14{\cdot}53,\ AR_D\ 14{\cdot}72,\ A\Delta_{\gamma-\alpha}\ 1{\cdot}440,\ A\Delta_{\beta-\alpha}\ 0{\cdot}870$$

DropBooks

Tin triphenyl ethyl crystallises from alcohol in centric groups of snow-white, highly refractive prisms, and from the molten crystals in large transparent plates, M.pt. 56° C. This and the preceding compound give a thick precipitate of a double compound of silver phenyl and silver nitrate with silver nitrate, which becomes black on warming. The density at 62° C. is 1·2953; $n_{H\alpha}$ 1·59917, n_D 1·60542, $n_{H\beta}$ 1·62236 at 62°.

From these figures :

$$\Sigma R_{H\alpha}\ 26{\cdot}38,\ \Sigma R_D\ 26{\cdot}61,\ \Sigma\Delta_{\beta-\alpha}\ 0{\cdot}820,\ MR_{H\alpha}\ 99{\cdot}96,$$
$$MR_D\ 100{\cdot}81,\ M\Delta_{\beta-\alpha}\ 3{\cdot}107$$

which give for tin in this compound,

$$AR_{H\alpha}\ 14{\cdot}69,\ AR_D\ 14{\cdot}86,\ A\Delta_{\beta-\alpha}\ 0{\cdot}917$$

Tin tricyclohexyl methyl occurs as a colourless, glycerine-like oil, B.pt. 221° C. at 15 mm. in a current of nitrogen, and forms a glassy mass when cooled to −75° C. It is miscible with benzene or ether in all proportions, insoluble in alcohol or water. Its density at 21·2° C. is 1·1945; $n_{H\alpha}$ 1·53379, n_D 1·53731, $n_{H\beta}$ 1·54628, $n_{H\gamma}$ 1·55384, at 21·2°.

Hence

$$MR_{H\alpha}\ 99{\cdot}632,\ MR_D\ 100{\cdot}180,\ M\Delta_{\gamma-\alpha}\ 3{\cdot}098,\ M\Delta_{\beta-\alpha}\ 1{\cdot}936$$

[1] This compound has more recently been prepared according to the following equation, the reaction being conducted in liquid ammonia: $NaSn(C_6H_5)_3 + CH_3I = CH_3Sn(C_6H_5)_3 + NaI$ (Bullard and Robinson, *J. Amer. Chem. Soc.*, 1927, **49**, 1368).

The atomic refraction and dispersion of tin in the compound is

$$AR_{H\alpha}\ 14{\cdot}461,\ AR_D\ 14{\cdot}642,\ A\Delta_{\gamma-\alpha}\ 1{\cdot}018,\ A\Delta_{\beta-\alpha}\ 0{\cdot}643$$

Tin tricyclohexyl ethyl is a very viscous oil, B.pt. 227° to 228° C. at 15 mm., with partial decomposition. Its density at 23·2° C. is 1·1766; $n_{H\alpha}$ 1·53453, n_D 1·53797, $n_{H\beta}$ 1·54700, $n_{H\gamma}$ 1·55459, at 20·2° C. These figures are for the distilled preparation, and a similar series is given for the non-distilled preparation. The figures for the atomic refraction and dispersion for tin in the compound are

$$AR_{H\alpha}\ 14{\cdot}477,\ AR_D\ 14{\cdot}664,\ A\Delta_{\gamma-\alpha}\ 1{\cdot}014,\ A\Delta_{\beta-\alpha}\ 0{\cdot}652.$$

Tin tribenzyl ethyl is formed by the interaction of tin tribenzyl chloride and magnesium ethyl bromide, the yield being almost theoretical. The product crystallises from alcohol-petroleum in colourless tablets, M.pt. 31° to 32° C., which are easily soluble in ether, benzene, or chloroform, less so in alcohol, and sparingly in light petroleum.

Aryl Derivatives of the Types $Alk.Alk'.SnAr_2$, $Alk.Alk'_2.SnAr$, Alk_2SnAr_2, *and* Alk_3SnAr.

Tin ethyl propyl dibenzyl.[1]—When tin ethyl tribenzyl in carbon tetrachloride solution is treated with 1 mol. of iodine, the following reaction takes place :—

$$Sn(C_2H_5)(CH_2.C_6H_5)_3+I_2=Sn(C_2H_5)(CH_2C_6H_5)_2I+C_6H_5CH_2I$$

The tin ethyl dibenzyl iodide thus obtained is then treated with magnesium propyl bromide, the ether distilled off, and the residue heated at 140° C. for one hour. After cooling, the mass is treated with water, and the oil thus formed dissolved in ether, the latter separated off, washed, and dried. On distillation, 70 per cent. of the oil distils at 220° to 225° C. at 15 mm., and is pure tin ethyl propyl dibenzyl. It does not solidify at 0° C., and is oxidised in the air at ordinary temperatures, whilst heating it under atmospheric pressure causes decomposition, with the separation of metallic tin. It is miscible with all the usual solvents. For the action of sulphuric acid on this compound, see tin diethyl dibenzyl.

Tin ethyl butyl dibenzyl.[2]—Tin ethyl dibenzyl iodide is treated with an excess of magnesium *n*-butyl bromide in ethereal solution, the ether distilled off, and the residue heated for one to two hours at 140° C. Distillation of the residue gives the required compound, boiling at 207° to 209° C. at 9 mm., or 175° to 180° C. at 3 to 5 mm. It is fairly soluble in benzene, less soluble in acetone and ether.

Tin ethyl dibutyl benzyl occurs as a by-product in the above preparation. It is a colourless liquid, B.pt. 175° to 180° C. at 9 mm., or 118° to 122° C. at 2·5 to 3 mm.

Tin dimethyl diphenyl.[3]—This is formed by treating disodium diphenyl stannide with methyl iodide in liquid ammonia. The yield is about 84 per cent.

Tin diethyl dibenzyl.—The product obtained from the interaction

[1] Smith and Kipping, *Trans. Chem. Soc.*, 1912, 101, 2553.
[2] Law, *J. Chem. Soc.*, 1926, p. 3243.
[3] Bullard and Robinson, *J. Amer. Chem. Soc.*, 1927, 49, 1368.

of tin dibenzyl chloride and magnesium ethyl bromide is an oil, which on distillation gives a fraction at 223° to 224° C. at 20 mm., corresponding to the desired compound. This oil, which is slightly decomposed on distillation, is heavier than water, does not solidify at ordinary temperatures, and is miscible with the usual organic solvents. On heating in air it rapidly decomposes with the separation of metallic tin, and oxidation by the air produces benzaldehyde.

When tin ethyl propyl dibenzyl or tin diethyl dibenzyl are treated with sulphuric acid or chlorsulphonic acid, no sulphonic acids can be obtained.

Tin trimethyl benzyl is prepared from sodium trimethyl stannide and benzyl chloride in liquid ammonia, according to the equation :

$$Me_3SnNa + C_7H_7Cl = Me_3SnC_7H_7 + NaCl$$

It decomposes when heated to 215° C.[1]

Tin trimethyl phenyl.[2]—Sodium trimethylstannide when treated with bromobenzene in liquid ammonia yields tin trimethyl phenyl, B.pt. 203° to 208° C., but the main product of reaction is tri (trimethylstannyl)-amine. This is formed according to the equation :

$$3NaSn(CH_3)_3 + 3C_6H_5Br + NH_3 = [Sn(CH_3)_3]_3N + 3C_6H_6 + 3NaBr$$

Tin trimethyl phenyl may also be prepared by the action of magnesium phenyl bromide on tin trimethyl bromide in benzene-ether solution. The yield by this method is 35 per cent. and the product distils at 203° to 208° C. It is a colourless oil, having a pleasant odour, and is converted by bromine to tin trimethyl bromide.

Tin triethyl phenyl[3] is obtained as an oil, B.pt. 254° C., from the reaction mixture derived from heating together tin triethyl iodide (1 mol.), bromobenzene (1 mol.), and metallic sodium. It forms a colourless liquid, which has to be distilled in hydrogen, since it is partially oxidised in the air, has a fairly pleasant odour, burns with a sooty flame, depositing metallic tin. It is highly refractive, and has a density 1·2639 at 0° C., is easily soluble in alcohol and ether, but insoluble in water. With alcoholic silver nitrate, iodine, fuming hydrochloric acid, and stannic chloride, the following reactions take place :—

$$2Sn(C_2H_5)_3(C_6H_5) + 2AgNO_3 = 2Sn(C_2H_5)_3NO_3 + C_{12}H_{10} + 2Ag$$
$$Sn(C_2H_5)_3(C_6H_5) + I_2 = Sn(C_2H_5)_3I + C_6H_5I$$
$$Sn(C_2H_5)_3(C_6H_5) + HCl = Sn(C_2H_5)_3Cl + C_6H_6$$
$$Sn(C_2H_5)_3(C_6H_5) + SnCl_4 = Sn(C_2H_5)_2Cl_2 + Sn(C_2H_5)(C_6H_5)Cl_2$$

Aryl Derivatives of the Type R_3SnX.

General Method of Preparation of Tin Triphenyl Halides.[4]—Tin tetraphenyl (85·4 grams) is dissolved in 700 grams of hot pyridine with mechanical stirring and the solution rapidly cooled in ice, so that a very fine suspension of the compound is produced. At a temperature of −48° C., 32 grams of bromine in 150 grams of pyridine are added in 6

[1] Kraus and Bullard, *J. Amer. Chem. Soc.*, 1926, 48, 2135.
[2] Bullard and Robinson, *loc. cit.*
[3] Ladenburg, *Annalen*, 1871, 159, 251.
[4] Krause, *Ber.*, 1918, 51, 913.

portions, with rapid stirring, and a clear yellow solution is obtained. The pyridine is distilled off and the bromobenzene removed *in vacuo*, leaving a thick, brown residue which is dissolved in ether, treated with hydrochloric acid to remove traces of pyridine, and any unchanged tin tetraphenyl filtered off. By shaking the ethereal solution with 30 per cent. sodium hydroxide, the halide is changed to the hydroxide, from which the halides may be obtained by the action of halogen acids. Yields 90 to 95 per cent.

Tin triphenyl chloride.—This has also been obtained by three other methods: (1) Tin diphenyl dichloride is treated with sodium amalgam in ether solution, or with ammonia.[1] (2) When an acetic acid solution of tin diphenyl dichloride is treated with sodium nitrite, 85 per cent. of the tin compound is converted to tin triphenyl chloride, nitrosobenzene also being formed.[2] (3) It occurs amongst other products, when tin tetraphenyl is decomposed by thallic chloride.[3] It crystallises from ether in colourless crystals, M.pt. 106° C., which are partly octahedral and partly prismatic. It boils at 240° C. at 13·5 mm., and is soluble in all the usual solvents.

Tin triphenyl bromide has more recently been prepared[4] by treating tin tetraphenyl in boiling chloroform with iodine, when tin triphenyl iodide is produced. This is then changed to the hydroxide by 30 per cent. sodium hydroxide, and the solution shaken with concentrated hydrobromic acid. Yield 50 per cent. This method obviates the cooling in solid carbon dioxide adopted by Krause.[5] It crystallises in millimetre-long pyramids or octahedra, and from dilute solution in fern-like masses. It melts at 120·5° C., and boils at 249° C. at 13·5 mm.

Tin triphenyl iodide forms large, four-sided, monoclinic prisms, M.pt. 121° C., B.pt. 253° C. at 13·5 mm.

Tin triphenyl fluoride[6] occurs as fine, snow-white prisms, M.pt. 357° C., becoming brown at 345° C. It is sparingly soluble in cold alcohol, ether, or water.

Tin tri-o-tolyl chloride crystallises from alcohol in thick, colourless prisms, M.pt. 99·5° C. The *bromide* forms compact, rhombic plates, M.pt. 99·5° C., and the *iodide* rhombic crystals, M.pt. 119·5° C. The solubilities of these three compounds are similar to the corresponding para compounds.

Tin tri-p-tolyl chloride forms rhombic plates, M.pt. 97·5° C., from hot alcohol. It is easily soluble in benzene or ether, sparingly in absolute alcohol. The *bromide* crystallises in colourless rhomboids, M.pt. 98·5° C., and has a similar solubility to the chloride. The *iodide* crystallises in a like form to the bromide and melts at 120·5° C., and has also a solubility similar to the chloride. The *fluoride* forms hair-fine needles, melting in a sealed tube at 305° C. to a brown liquid. It is readily soluble in alcohol, but insoluble in ether.

Tin tri-m-xylyl fluoride is deposited as fine, matted needles from hot benzene, M.pt. 209° C., somewhat soluble in warm ether and alcohol. The other halides have not been obtained in a crystalline form.

Tin tri-p-xylyl fluoride forms fine, microscopic needles, melting

[1] Aronhelm, *Annalen*, 1878, 194, 145.
[2] Aronhelm, *Ber.*, 1879, 12, 509.
[3] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 256.
[4] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, 48, 1054.
[5] Krause, *Ber.*, 1918, 51, 913.
[6] Krause and R. Becker, *Ber.*, 1920, 53, [B], 183,

in a closed tube at 247° C. (corr.). It is somewhat soluble in boiling ether and boiling alcohol. The *chloride* crystallises from hot alcohol in compact columns, M.pt. 141·5° C., very easily soluble in benzene or chloroform, readily in boiling ether, sparingly in hot alcohol, insoluble in cold alcohol. The *bromide* forms compact, six-sided crystals, M.pt. 151° C. (corr.), and is more soluble than the chloride. The *iodide* yields colourless, clear, six-sided plates from ether-alcohol, M.pt. 159·5° C. (corr.), less soluble than the chloride.

Tin tricyclohexyl fluoride [1] is obtained by treating the base with dilute hydrofluoric acid, or the bromide with neutral potassium fluoride, in boiling aqueous alcoholic solution. It is sparingly soluble in all the usual solvents. When heated with acetic acid it is converted into the *acetate*, six-sided prisms, decomposing at 305° C. The *chloride* crystallises in prismatic plates, M.pt. 129° to 130° C., decomposing at about 286° C., and having a similar solubility to the bromide. With dry ammonia it forms $(C_6H_{11})_3SnCl.2NH_3$, M.pt. 128° C. The *bromide* is obtained by adding the requisite quantity of bromine to ice-cooled tin tetracyclohexyl, and removing the cyclohexyl bromide which is formed by heating on a boiling water-bath at 15 mm. The crude product is triturated with a little cold 94 per cent. alcohol and recrystallised from a little hot alcohol. It melts at 77° C., and decomposes at about 280° C. It crystallises in thick prisms, a centimetre in length, very easily soluble in benzene, chloroform, or ether, easily in hot alcohol. The *iodide* is prepared from the tetracyclohexyl compound by the action of iodine in benzene solution at room temperature. It crystallises from alcohol in colourless, six-sided plates, M.pt. 65° C., decomposing at about 290° C. In the dark the compound remains colourless, but becomes yellow on exposure to light.

The *hydroxide* is formed from the bromide by shaking its ethereal solution with an excess of 15 per cent. potassium hydroxide. From alcohol it forms six-sided columns which melt rather indefinitely at 220° to 222° C.

Tin tribenzyl chloride.[2]—The first preparation of this compound was made by adding stannic chloride (1 mol.) to ice-cold magnesium benzyl chloride (3 mols.) in dry ether, but the yield was poor. In Kipping's method the stannic chloride and magnesium are mixed in dry ether, prior to the addition of the benzyl chloride, this method giving a 60 per cent. yield. The crude product is recrystallised from acetone, and then from glacial acetic acid, until the melting-point is constant. It forms well-defined prisms, M.pt. 143° to 145° C., readily soluble in acetone, benzene, or chloroform, less so in ether or alcohol, and insoluble in water. With 1 mol. of iodine it reacts as follows :—

$$2Sn(CH_2C_6H_5)_3Cl+2I_2=Sn(CH_2C_6H_5)_2Cl_2+Sn(CH_2C_6H_5)_2I_2+2C_6H_5CH_2I$$

Aryl Derivatives of the Types R_2SnX_2 *and* R_2SnXX'.

Tin diphenyl dichloride, $Sn(C_6H_5)_2Cl_2$.[3]—Formed: (1) By the interaction of tin tetraphenyl (1 mol.) and stannic chloride (1 mol.) in boil-

[1] Krause and Pohland, *Ber.*, 1924, 57, [B], 535.
[2] Pfeiffer and Schnurmann, *Ber.*, 1904, 37, 319; Smith and Kipping, *Trans. Chem. Soc.*, 1912, 101, 2553.
[3] Aronheim, *Annalen*, 1878, 194, 145.

ing xylene. (2) Mercury diphenyl is mixed with an equal weight of stannic chloride, the mixture covered with light petroleum, and digested in a paraffin-bath for twelve hours. The whole is then poured into water, the petroleum drawn off, and the aqueous solution heated from 85° to 90° C. on the water-bath. An oil separates out, and this on standing solidifies to a mass of white crystals of tin diphenyl dichloride. (3) By the interaction of tin tetraphenyl and thallic chloride.[1] The compound forms colourless, triclinic prisms, M.pt. 42° C., B.pt. 333° to 337° C., with partial decomposition. It is easily soluble in ether, alcohol, or petroleum, sparingly soluble in water, but tends to decompose in the latter. With strong acids it yields stannic chloride and benzene. If the aqueous solution from which the above tin diphenyl dichloride is obtained is heated for a long period, tin diphenyl hydroxychloride and tin diphenyl oxide are formed. They may be converted to the dichloride by treatment with hydrochloric acid. For the *difluoride*, see p. 326.

Tin diphenyl hydroxychloride.—As indicated above, this product is obtained by the action of water on the dichloride. It melts at 187° C., and at higher temperatures develops an odour of diphenyl, gives the dichloride on warming with concentrated hydrochloric acid, and forms acid and basic salts of the type $SnPh_2ClX$, these readily being produced by the action of hydrogen chloride, bromide, or iodide. The hydroxychloride is an amorphous powder, which is insoluble in the usual organic solvents.

Tin diphenyl chloro-iodide,[2] $Sn(C_6N_5)_2ClI$.—The best yield is obtained by treating the chloride with hydrogen iodide:

$$Sn(C_6H_5)_2Cl_2+HI=HCl+Sn(C_6H_5)_2ClI$$

It crystallises from anhydrous ether in transparent prisms, M.pt. 69° C., water or heat rapidly decomposing the compound. The corresponding *chlorobromide*, M.pt. 39° C., is easily soluble in alcohol, ether, carbon bisulphide, or ligroin, but some difficulty is encountered in getting the body to solidify.

Tin diphenyl dibromide.—Formed by the action of hydrogen bromide on tin diphenyl oxide, the oil solidifying instantly on the addition of a crystal of the chlorobromide. The compound has been more recently prepared by the direct bromination of tin tetraphenyl.[3] It resembles the chlorobromide in properties, and melts at 38° C. *Tin diphenyl di-iodide* does not appear to be stable, the reaction taking the following course:—

$$1.\ Sn(C_6H_5)_2O+2HI=Sn(C_6H_5)_2I_2+H_2O$$
$$2.\ Sn(C_6H_5)_2I_2+2HI=SnI_4+2C_6H_6$$

Tin diphenyl oxide.[4]—When the corresponding chloride or hydroxychloride in aqueous solution is digested with alkalies, or alcoholic or aqueous solutions of the chloride are treated with potassium or sodium hydroxides, ammonia or ammonium carbonate, the oxide is precipitated as a white powder, which resembles the hydroxychloride in solubility and properties. It does not melt, and decomposes without fusion on heating.

Tin diphenyl diethoxide, $Sn(C_6H_5)_2(OC_2H_5)_2$.—If sodium ethyl-

[1] Goddard, Ashley, and Evans, *Trans. Chem. Soc.*, 1922, 121, 978.
[2] Aronheim, *Annalen*, 1878, 194, 145.
[3] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, 48, 1054.
[4] Aronheim, *loc. cit.*

ate be treated with tin diphenyl dichloride a precipitate is immediately thrown down. This consists of tin diphenyl oxide and sodium chloride, and if it be filtered off, and the filtrate evaporated, small white crystals of the ethoxide are deposited. These are best purified by repeated solution in alcohol and evaporation over sulphuric acid. The reaction is represented thus :

1. $Sn(C_6H_5)_2Cl_2+2NaOC_2H_5=2NaCl+Sn(C_6H_5)_2(OC_2H_5)_2$
2. $Sn(C_6H_5)_2Cl_2+2NaOC_2H_5=2NaCl+Sn(C_6H_5)_2O+(C_2H_5)_2O$

Tin diphenyl aminochloride, $Sn(C_6H_5)_2NH_2Cl$, is formed as a by-product in the preparation of tin triphenyl chloride from tin diphenyl chloride by the action of ammonia. When treated with water it is decomposed into tin diphenyl hydroxychloride and ammonia.

Tin dibenzyl dichloride.[1]—When tin tribenzyl chloride (1 mol.) is dissolved in carbon tetrachloride, and iodine (1 mol.) added in small quantities, the following reaction ensues :—

$$2Sn(CH_2C_6H_5)_3Cl+2I_2=Sn(CH_2C_6H_5)_2Cl_2+Sn(CH_2C_6H_5)_2I_2+2C_6H_5CH_2I$$

By suitable treatment this mixture is then converted to chloride, which is easily soluble in alcohol, acetone, ether, chloroform, carbon tetrachloride, or boiling acetic acid, sparingly soluble in hot, light petroleum. It forms long needles, M.pt. 163° to 164° C. *Tin dibenzyl diiodide* is more soluble in carbon tetrachloride than the corresponding chloride, so that it can be obtained from the mother-liquors from which the chloride has been deposited. It is also formed when tin dibenzyl oxide is dissolved in hot acetone containing hydrogen iodide. The compound crystallises in long, silky, yellow needles, M.pt. 86° to 87° C. The *dibromide* is formed from the oxide in a similar manner to the iodide. It is more soluble than the chloride, and crystallises in colourless needles from light petroleum, M.pt. 103° C.

Tin dibenzyl diacetate is deposited from the solution obtained by dissolving tin dibenzyl oxide in glacial acetic acid. It forms long, colourless needles, M.pt. 136° to 137° C., readily soluble in acetone, chloroform, alcohol, or benzene.

Tin dicyclohexyl difluoride[2] is prepared from the dibromide or dichloride by adding the calculated amount of neutral potassium fluoride in aqueous alcoholic solution. It is a fine, white, crystalline powder, difficultly soluble in all solvents with the exception of hot acetic acid, from which it crystallises in bushy needles, M.pt. 278° C., with previous sintering. The *dichloride* is obtained from the dihydroxide by long warming with concentrated hydrochloric acid. It crystallises from benzene in colourless needles, M.pt. 88° to 89° C., which sometimes are a centimetre in length. When molten, it becomes turbid at about 220° C., and decomposes with rise of temperature. The dichloride, like the dibromide, is hydrolysed by a large bulk of water. Prolonged boiling of tin tetracyclohexyl in chloroform or carbon tetrachloride solution with the calculated quantity of bromine yields the *dibromide*, which crystallises in needles, M.pt. 58° C. It is very readily soluble in chloroform, benzene, or carbon tetrachloride, sparingly in alcohol or ether.[3] The

[1] Smith and Kipping, *Trans. Chem. Soc.*, 1912, 101, 2553.
[2] Krause and Pohland, *Ber.*, 1924, 57, [B], 535.
[3] See Grüttner, *Ber.*, 1914, 47, 3257.

di-iodide is a snow-white, crystalline powder, M.pt. 42° C.[1] Heated in a sealed tube it gives a clear liquid at about 250° C., at 253° C. it becomes cloudy and changes to dark red, and above 300° C. becomes black. The *dihydroxide* is formed by the hydrolysis of the dibromide, and a basic bromide is not obtained. The dihydroxide is a white, amorphous powder, insoluble in water and the usual organic solvents. It discolours towards 280° C., sinters at 287° C., and is completely decomposed at 291° C.

Aryl Derivative of the Type $Alk.Ar.SnX_2$.

Tin ethyl phenyl dichloride,[2] $Sn(C_2H_5)(C_6H_5)Cl_2$, is prepared by the action of stannic chloride on tin triethyl phenyl. It forms rhombic plates, M.pt. 45° C., easily soluble in ammonia and alcohol, but with difficulty in water or dilute hydrochloric acid.

Aryl Derivatives of the Type R_2Sn.[3]

Tin diphenyl.—To the Grignard solution from 75 grams of bromobenzene in 400 c.c. of ether, 15 grams of anhydrous, finely powdered stannous chloride are added, the mixture being shaken, ice-cooled, and dry nitrogen gas passed in. The solution first becomes deep reddish-brown, and as the reaction proceeds a golden yellow, amorphous powder separates out. After one hour at room temperature the mixture is gently warmed for ten minutes, all operations being conducted in a nitrogen atmosphere. The product is then decomposed by ice, and shaken with benzene, and the benzene-ether layer removed, dried, and evaporated *in vacuo* to about 70 c.c. The deep red solution is shaken with alcohol, tin diphenyl being precipitated as a yellow powder. This may be purified by solution in benzene and precipitation with alcohol, the final product being washed with alcohol, then rapidly with a little ether, and dried *in vacuo* over phosphorus pentoxide. Yield 16 grams, 64 per cent. It is a shining yellow, amorphous powder, readily soluble in benzene and chloroform, easily in ether, and insoluble in alcohol. Very dilute benzene solutions are intense yellow to reddish yellow, and soon become turbid on exposure to air, owing to oxidation. In sunlight the benzene solutions become deep red and a bright yellow precipitate separates. Dry tin diphenyl is oxidised in the air, becoming white. Fuming nitric acid causes it to inflame, and alcoholic silver nitrate is reduced. It softens at 126° C., and melts to a dark red liquid at 130° C., from which tin separates at 205° C. When brominated at −25° C. in chloroform solution an oil is produced, and this, with aqueous alcoholic potassium fluoride solution, gives *tin diphenyl difluoride*, quadratic columns, melting above 360° C. It is slightly soluble in alcohol or benzene.

Tin di-p-tolyl is an orange-yellow, amorphous powder, softening at 109° C., and melting to a clear, dark red liquid at 111·5° C.; on further heating it becomes turbid, and tin separates out at 245° C. It dissolves in benzene in all proportions, readily in ether, but is insoluble in alcohol. The solutions resemble potassium dichromate in colour, and blacken alcoholic silver nitrate. It is not so readily oxidised in air as the phenyl compound.

[1] Grüttner, M.pt. 145° C.

[2] Ladenburg, *Annalen*, 1871, 159, 251.

[3] Krause and R. Becker, *Ber.*, 1920, 53, [B], 183; Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, 48, 1054; see p. 329.

Tin di-p-xylyl has similar properties to the preceding compounds. It sinters at 155° C., forms a deep red liquid at 157° C., and decomposes at 240° C.

Tin di-cyclohexyl[1] is an intense yellow, odourless powder, very easily soluble in benzene, soluble in ether, and insoluble in absolute alcohol. In very dilute benzene solution it is citron yellow. When heated in absence of air it becomes deep orange-yellow at 130° C., and melts to a ruby red liquid at 176° to 178° C., darkening at 260° C., and decomposing at 285° C.

Tin di-α-naphthyl is prepared in the usual manner, 30 grams of α-bromonaphthalene and 5 grams of stannous chloride giving 8 grams of tin dinaphthyl, 73 per cent. It softens at 196° C., melts to a dark red liquid at 200° C., and decomposes at 255° C.

Aryl Derivatives of the Types $Ar_3Sn.SnAr_3$ and $Ar_3Sn.SnAlk_3$.[2]

Hexaphenyldistannane.—The preparation is carried out in the same manner as that of tin diphenyl, but instead of warming the product for ten minutes as stated in that preparation, it is now vigorously boiled for three to four hours in a stream of nitrogen. The reaction product is decomposed with water, extracted with benzene, and the latter solution separated off and dried. Hexaphenyldistannane may also be obtained by the reduction of tin triphenyl chloride in benzene-xylene solution by metallic sodium (yield 50 per cent.), or in alcoholic solution (yield 65 per cent.). From benzene it contains 1·5 mols. of benzene of crystallisation, but from ether flat rectangular plates are deposited, from chloroform, pyramids. It is somewhat soluble in benzene, readily in chloroform, sparingly in ether or acetone, and insoluble in alcohol. It melts at 237° C., becomes yellow at 250° C., and decomposes at 280° C. It reduces silver solutions at —75° C. to black metallic silver. Bromination at —30° C. produces tin triphenyl bromide.

Hexa-p-tolyldistannane is prepared by the treatment of tin tri-p-tolylbromide with metallic sodium and alcohol. Yield 64 per cent. It crystallises from benzene in colourless, rhombic plates, easily soluble in benzene or ether, sparingly in alcohol. It melts at 143·5° C., becomes yellow at 285° C., and decomposes at 335° C. It has similar properties to the phenyl compound.

Hexabenzyldistannane,[3] $(C_6H_5.CH_2)_3Sn.Sn(C_6H_5.CH_2)_3$, is prepared by heating tin tribenzyl chloride with sodium in toluene solution. It separates from acetone in colourless tablets, M.pt. 147° to 148° C., readily soluble in hot acetone or benzene. Treatment with iodine in benzene solution yields tin tribenzyl iodide.

Hexa-p-xylyldistannane[4] is obtained from the bromide in 50 per cent. yield. It crystallises from benzene-alcohol in flat, rhombic plates, very soluble in benzene or chloroform, sparingly soluble in ether, and insoluble in alcohol. It melts at 196° C. (corr.), becomes yellow at 350° C., and decomposes at 368° C.

Hexacyclohexyldistannane[5] is prepared from the bromide in

[1] Krause and Pohland, *Ber.*, 1924. 57, [B], 536.
[2] Krause and Becker, *loc. cit.*
[3] Law, *J. Chem. Soc.*, 1926, p. 3243.
[4] Krause and R. Becker, *loc. cit.*
[5] Krause and Pohland, *loc. cit.*

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xylene solution, in 90 per cent. yield. It crystallises from hot xylene or benzene in six-sided plates, decomposing above 300° C. It is sparingly soluble in cold benzene or xylene, easily soluble on warming, and is insoluble in alcohol or ether.

Triphenyltrimethyldistannane,[1] $Ph_3Sn.SnMe_3$.—Sodium tin triphenyl is treated with tin trimethyl bromide in liquid ammonia, when the product is immediately precipitated. It melts sharply to a clear, colourless liquid at 106° C., and shows no tendency to oxidise in air.

Derivatives of Tin Triphenyl.[2]

Sodium tin triphenyl, $(C_6H_5)_3SnNa$.—Tin triphenyl bromide is dissolved in liquid ammonia and the solution treated with metallic sodium. The reaction occurs immediately, the product being formed together with sodium bromide. The compound is a pale yellow, amorphous powder, soluble in liquid ammonia, giving a pale yellow solution, and it dissolves to some extent in dry ether. When dry oxygen is passed through its solution in liquid ammonia, the solution evaporated and the residue extracted with hot benzene, tin triphenyl hydroxide, tin tetraphenyl, and tin diphenyl oxide are formed. The reaction between sodium tin triphenyl and phenylmercuric iodide in liquid ammonia gives rise to tin triphenyl, sodium iodide, mercury, and phenylmercuric amine, $C_6H_5.Hg.NH_2$, M.pt. 123·5° to 124° C. With sodium monochloracetate in liquid ammonia solution the reaction is as follows :—

$$(C_6H_5)_3SnNa + CH_2Cl.COONa = (C_6H_5)_3SnCH_2COONa + NaCl$$

The tin compound thus formed crystallises in plates, M.pt. 122° to 122·5° C., soluble in the usual organic solvents, save petroleum ether, and insoluble in water. It is best crystallised from 80 per cent. acetic acid, as the sodium salt is very soluble in water and undergoes hydrolysis.

Tin triphenyl hydride is formed according to the following equation :

$$(C_6H_5)_3SnNa + NH_4Br = (C_6H_5)_3SnH + NaBr + NH_3$$

Five grams of tin triphenyl bromide are placed in a reaction tube and 50 c.c. of liquid ammonia condensed upon it. Sodium is added gradually until a permanent blue colour is obtained (0·63 gram sodium). Ammonium bromide, 1·25 grams, is added, the colour disappears and a white precipitate forms. The ammonia is evaporated and the residue extracted with ether. On evaporating the ether in an atmosphere of ammonia, a cloudy yellow oil and a white crystalline solid, M.pt. 229° to 232° C., are obtained. This solid is *tin triphenyl*, and the liquid in an ammonia atmosphere boils at 173° to 174° C. at 6 mm. The latter is the hydride, which may be oxidised to tin triphenyl (M.pt. 232·5° C.) by passing dry oxygen through its solution in absolute alcohol for fifteen minutes. A white crystalline powder is obtained, which may be recrystallised from ether. All manipulations of the hydride must be conducted in an inert atmosphere. When the hydride is treated with sodium in liquid ammonia, sodium tin triphenyl is formed, and when tin triphenyl chloride is added to the solution, tin triphenyl and sodium chloride result.

[1] Krause and Bullard, *J. Amer. Chem. Soc.*, 1926, 48, 2134.
[2] Chambers and Scherer, *J. Amer. Chem. Soc.*, 1926, 48, 1055.

Tin diphenyl hydride is prepared in much the same way as the preceding compound, the reactions being carried out in liquid ammonia, and represented by the following equations :—

$$(C_6H_5)_2SnBr_2 + 4Na = (C_6H_5)_2SnNa_2 + 2NaBr$$
$$(C_6H_5)_2SnNa_2 + 2NH_4Br = (C_6H_5)_2SnH_2 + 2NaBr + 2NH_3$$

The compound forms as a dark brown precipitate. The ammonia is allowed partially to evaporate and dry ether added. The remainder of the ammonia is then evaporated, and by means of a eudiometer connected to the reaction tube, it is found that hydrogen corresponding to one molecular equivalent is evolved, *i.e.* the hydride loses its hydrogen, yielding *tin diphenyl*. The latter compound by this process is obtained as a yellow solid, decomposing at 205° C., and readily soluble in organic solvents, except ethyl alcohol. In the solid state it is not readily oxidised in the air, but in solutions the oxide soon separates. This compound differs from that described by Krause [1] in its melting-point and reactivity towards oxygen (p. 326).

Tin tetraphenyl reacts with sodium in liquid ammonia to form sodium tin triphenyl and disodium tin diphenyl, the amounts depending on the conditions of the experiment.

Heterocyclic Systems containing Tin.

These compounds are similar to the heterocyclic compounds of lead. Tin dimethyl or diethyl-cyclopentamethylene is obtained by the action of tin dimethyl- or diethyl dibromide or di-iodide on the magnesium compound of 1 : 5-dichloropentane with difficulty, and has the following constitution :—

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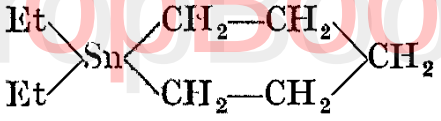
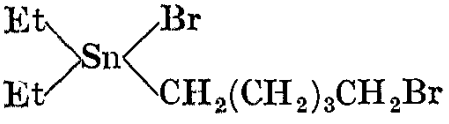
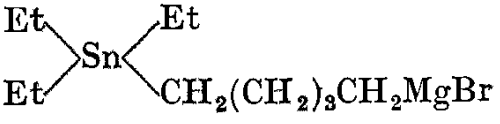


It is analogous to the cyclohexanes, in which a carbon atom has been replaced by quadrivalent tin. The constitution of the body is completely determined by scission with halogen and molecular weight determinations. By the action of two atoms of bromine in the cold the ring is partially split, and tin diethyl-5-bromoamyl bromide obtained.



The reaction is quantitative and analogous to that of the lead compound.

By the action of ethyl magnesium bromide, the bromine atom bound to the tin is replaced by the ethyl group, with the formation of tin triethyl-5-bromoamyl. In absolute ether solution the reaction with magnesium goes quite easily, a 75 per cent. yield being obtained, the (5-triethylstannyl-n-amyl)-magnesium bromide,



giving with water, tin triethyl-n-amyl.

[1] Krause and R. Becker, *Ber.*, 1920, 53, [B], 183.

By the action of lead trimethyl bromide on the magnesium compound of trimethyl-5-bromoamyl tin, 1-trimethylstannyl-5-trimethylplumbyl-n-pentane is formed.

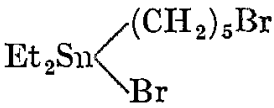
Lead trimethyl bromide and tin triethyl bromide with the magnesium compound of 1 : 5-dichloropentane give bis-trimethylplumbyl-n-pentane and bis-triethylstannyl-n-pentane respectively.

Tin diethyl-cyclopentamethylene,

$$Et_2Sn{<}(CH_2)_5$$

To the magnesium compound from 112 grams of 1 : 5-dichloropentane in 400 c.c. of dry ether, 130 grams (half the calculated quantity) of tin diethyl dibromide are added in small portions with shaking. A violent reaction takes place and all the products pass into solution. After the reaction has subsided the whole is boiled for thirty minutes, the ether distilled off, and the residue baked on a boiling water-bath for one hour. The mass is decomposed with water, the ether layer separated, washed with water, and dried over calcium chloride. Removal of the ether gives an oil, which is fractionated under reduced pressure in a stream of carbon dioxide. The fraction distilling at 98° to 104° C., after several distillations at 14 mm. pressure, gives a constant boiling fraction at 95° C. Yield about 25 grams. The compound is a thin, colourless oil having a pleasant smell, resembling pine-leaf extract. In absence of air it may be kept for a month, but in the course of a day becomes turbid in air, depositing a white resin.

Tin diethyl-5-bromoamyl bromide,



A solution of 12·3 grams of the preceding compound in 50 c.c. of ethyl acetate is cooled in ice and treated dropwise with 8 grams of bromine in 25 c.c. of ice-cold ethyl acetate, the mixture being frequently shaken. When all the bromine has been added, the ethyl acetate is distilled off, and the oil fractionated in carbon dioxide. The fraction, B.pt. 189° to 192° C. at 16 mm., gives a thick, colourless oil, B.pt. 190·5° C. at 16 mm. Yield quantitative. The bromine atom bound to the tin may be removed by treating the alcoholic solution of the substance with alcoholic silver nitrate containing some nitric acid. The second bromine atom is estimated by the method of Carius.

Tin triethyl-5-bromoamyl, $Et_3Sn.(CH_2)_5Br$.—Fifteen grams of tin diethyl-5-bromoamyl bromide in 200 c.c. of ether are added to the Grignard solution from 25 grams of ethyl bromide in 100 c.c. of ether. The reaction is completed by boiling the mixture for five minutes. The mass is decomposed with water, and the ether layer separated and dried. Distillation in a carbon dioxide atmosphere yields an oil, B.pt. 155·5° C. at 15 mm. Yield quantitative. It is a colourless, thin, air-stable, almost odourless oil.

Tin triethyl-n-amyl, and 1 : 10-Bis-triethylstannyl-n-decane, $Et_3Sn.(CH_2)_{10}.SnEt_3$.—Magnesium powder, 1·5 grams, is cauterised with 0·5 gram of ethyl bromide in 10 c.c. of ether. The ether is then poured off and the powder treated several times with ether, the latter being decanted off. A solution of 10 grams of tin triethyl-5-bromoamyl in 40 c.c. of ether is then added to the powder and a violent reaction takes

place. This is completed by two hours' boiling. The ether solution is then poured off, decomposed with water, and the ether layer separated and dried. The solution is now distilled in carbon dioxide under reduced pressure. At 111° C. at 15 mm. 6 grams of tin triethyl-n-amyl are obtained, and at 247° to 249° C. at 15 mm. 2 grams of 1 : 10-bis-triethylstannyl-n-decane. The latter is a colourless, odourless oil.

Tin diethyl-n-amyl bromide is obtained as a colourless, thick, unpleasant smelling oil, by adding the requisite quantity of bromine in ethyl acetate to tin triethyl-n-amyl.

Tin dimethyl-cyclopentamethylene is prepared in the same manner as the corresponding ethyl compound, which it resembles in properties. When treated with bromine it yields *tin dimethyl-5-bromoamyl bromide*, a colourless, air-stable, somewhat viscous, pungent oil of unpleasant odour.

Tin trimethyl-5-bromoamyl, prepared in the usual way, is a colourless, thin, air-stable oil, having an odour resembling the tin alkyls.

1 : 5-Bis-triethylstannyl-n-pentane, $Et_3Sn.(CH_2)_5.SnEt_3$. — Fifty grams of tin triethyl bromide are added to the Grignard solution from 15 grams of 1 : 5-dichloropentane in 150 c.c. of ether. The reaction takes place smoothly and is completed by three hours' warming; the solution is decomposed with water, the ethereal layer dried and the solvent removed. At 14 mm. the product distils at 204° to 206° C., further distillations giving a pure compound at 205·5° C. Yield 12 grams.

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Derivative containing Tin and Lead.

1-Trimethylstannyl-5-trimethylplumbyl-n-pentane, $Me_3Sn.(CH_2)_5.PbMe_3$. —The magnesium compound from 9·2 grams of tin trimethyl-5-bromoamyl in 50 c.c. of ether is shaken with 9·8 grams of lead trimethyl bromide. A smooth reaction takes place and all the product dissolves. The whole is boiled for thirty minutes and decomposed with water. To remove the excess of lead trimethyl bromide, the ethereal solution is twice shaken with 20 per cent. potassium hydroxide and 10 per cent. sulphuric acid, and the precipitated lead trimethyl sulphate filtered off. The ethereal solution is then washed with water, dried over calcium chloride, and the ether distilled off. The oil remaining, when distilled under reduced pressure gives 7 grams of product at 164° C., this after several distillations yielding 4·5 grams of the required compound as a thick, colourless oil, B.pt. 162° C. at 17·5 mm.

The physical constants of the above compounds are shown in Table XVIII. of the Appendix.

CHAPTER XIV.

ORGANOMETALLIC DERIVATIVES OF LEAD.

A PERIOD of seven years elapsed after the preparation of the first tin organic compound before a derivative of lead was obtained. In 1859 Buckton isolated lead tetraethyl by the interaction of zinc ethyl and lead chloride. A number of investigators then worked upon this com-

TABLE I.

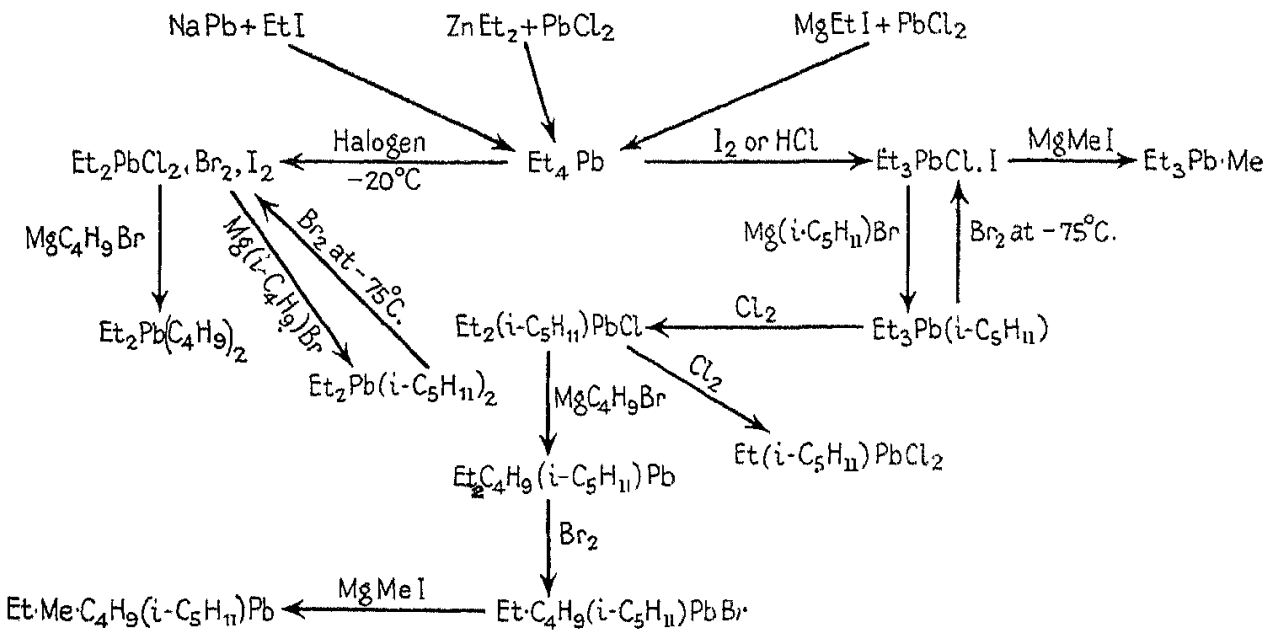
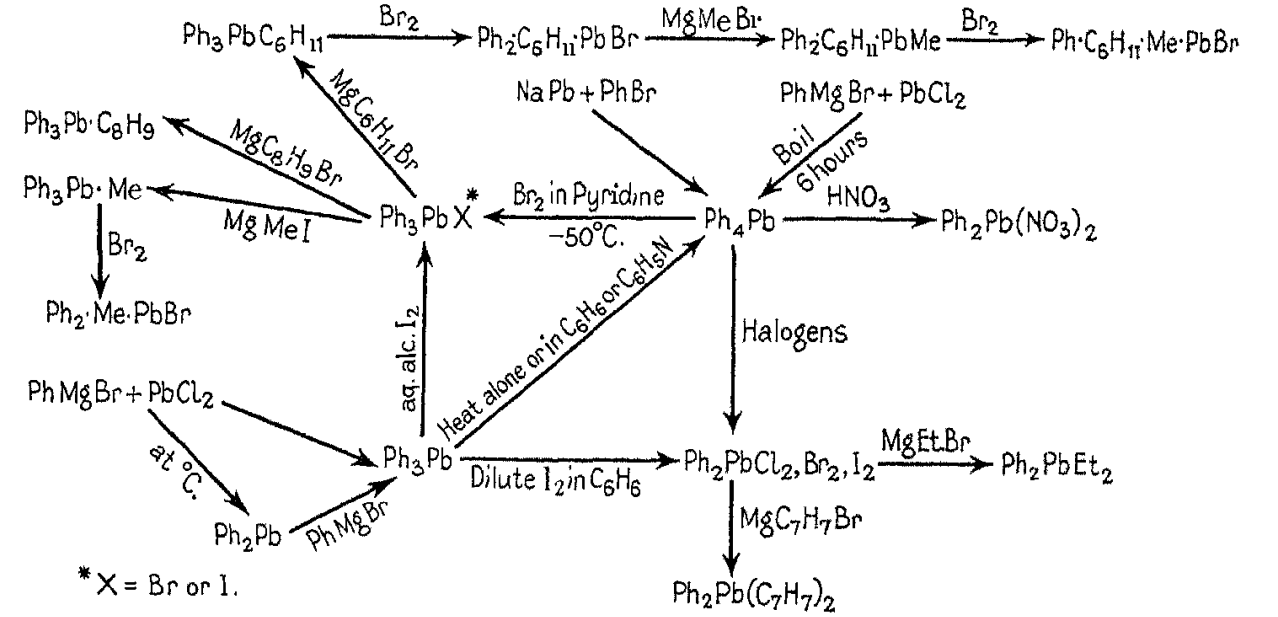


TABLE II.



pound together with lead tetramethyl, and produced many derivatives of the type R_3SnX (R=alkyl; X=acid radicle). It is, however, within the last ten years that the majority of the products recorded in this chapter have been made. The bulk of the work centres round mixed alkyl or aryl compounds, or combinations of the two. The above tables have been drawn up to show the main reactions carried out. In I. the lead alkyls are illustrated by making use of some ethyl derivatives, and in II. phenyl compounds are used. The heterocyclic compounds of lead are similar to those of tin.

Alkyl Derivatives of the Type R_4Pb.

Lead tetramethyl, $Pb(CH_3)_4$.—This may be prepared by the interaction of a sodium-lead alloy (20 per cent. sodium) and methyl iodide,[1] or from lead chloride and zinc methyl.[2] It has more recently been obtained by the Grignard reagent, from magnesium methyl chloride and lead chloride.[3] The compound is a liquid boiling at 110° C., melting at −27·5° C., insoluble in water, but readily soluble in alcohol or ether. The following physical constants have been determined: density 2·034; 1·9951; $n_F - n_C$ 0·01881. Treatment with hydrochloric acid or iodine removes one of the methyl groups, giving a lead trimethyl halide.

Lead tetraethyl is isolated in a similar manner to the above methyl compound, from sodium-lead alloy and ethyl iodide[4] or from lead chloride and zinc ethyl.[5] A simpler method than the foregoing is carried out as follows:[6] Twenty grams of ethyl iodide and 3 grams of magnesium are allowed to react in dry ether, and 10 grams of lead dichloride added, the whole then boiled for one hour. The mixture is then decomposed with water, the ether layer removed and dried over calcium chloride. After distilling off the ether, lead tetraethyl remains as a colourless oil, boiling with decomposition about 200° C., but undecomposed at 91° to 92° C. at 19 mm. or 83° C. at 13 mm. It has recently been obtained in 90 per cent. yield by the interaction of zinc diethyl and lead chloride.[7] The compound is insoluble in water, but miscible with ether. One ethyl group is split off by the action of hydrochloric acid or iodine, and sulphur dioxide yields diethyl sulphone. The compound is now used industrially for mixing with the fuel of explosion motors, as it allows greater compression without the danger of self-ignition.[8] Physical constants: density. 1·62; 1·6591; 1·64296 at 22·4° C., n_α 1·50934, n_D 1·51417, n_γ 1·53430, $n_F - n_C$ 0·01750.

Lead tetra-n-propyl is obtained by the interaction of magnesium propyl bromide and lead chloride. Density 1·4419; $n_F - n_C$ 0·01566.

Lead tetra-sec-propyl is a highly mobile liquid, B.pt. 120·0° C. at 14 mm., having a density 1·4578 at 12° C.

Lead tetra-isobutyl occurs as white plates, M.pt. −23° C., density 1·3240 at 20·2° C.

Lead tetra-isoamyl has a density of 1·2332 at 20·5° C.

[1] Cahours, *Annalen*, 1862, 122, 67.
[2] Butlerow, *Jahresber.*, 1863, p. 476.
[3] Grüttner and Krause, *Ber.*, 1916, 49, 1415.
[4] Ghira, *Gazzetta*, 1894, 24, i. 44.
[5] Buckton, *Annalen*, 1859, 109, 222; 1861, 112, 226; Frankland and Lawrance, *Trans. Chem. Soc.*, 1879, 35, 245.
[6] Pfeiffer and Truskier, *Ber.*, 1904, 37, 1128.
[7] Meyer, *Chem. News*, 1925, 131, 1.
[8] Jolibois and Normand, *Compt. rend.*, 1924, 179, 27.

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Alkyl Derivatives of the Type R_3PbR'.[1]

The method of preparation of this type of compound consists in treating lead trialkyl halides with magnesium alkyl halides, the reaction proceeding smoothly, and giving 90 to 95 per cent. yields. These bodies are colourless, easily mobile, and extraordinarily volatile—the trimethyl series at ordinary pressures soon becoming undecomposed boiling liquids, and in the pure state they can be kept in contact with air for a month without decomposing, provided that the light is excluded. In sunlight or direct daylight, however, they soon give brown precipitates, and the separation of metallic lead has been noticed. To ensure the production of pure compounds, the Grignard reagent must only be in slight excess, and the trialkyl lead halide must be free from lead halide. The separation of the mixed lead alkyls from their reaction products is carried out simply in the following manner: At the first distillation, the compounds of the triethyl series come over almost entirely, and the first and second runnings are quite distinct within a few degrees. These mixed compounds resemble the simple lead alkyls in their properties, and at very low temperatures solidify to glassy, amorphous masses. They immediately reduce alcoholic silver nitrate, and with halogens all the compounds, with the exception of lead methyl triethyl, split off a methyl or ethyl group. The compounds thus formed of the type $Me_2.Alk.Pb.Hal.$, form important starting-points for the preparation of mixed lead tetra-alkyls of the types $Me_2.Pb.Alk._2$ and $Me_2.Pb.Alk'.Alk.$ The bodies are highly poisonous, and possess a fruity smell, sometimes resembling raspberries, but the smell may be concealed by certain radicles, such as the isoamyl.

Lead trimethyl ethyl.—To the magnesium compound from 13·5 grams of ethyl bromide (0·125 mol.) in absolute ether, 28·8 grams of lead trimethyl chloride or 33·2 grams of lead trimethyl bromide are added, and after the initial reaction has subsided the whole is heated for two hours on the water-bath. The thick paste thus obtained is decomposed by water, the flask being cooled in ice, and the ether separated off. One quarter of the volume of the latter is distilled off, and the remainder fractionally distilled, the receiver being cooled in carbon dioxide-ether mixture. The yield is 85 per cent., and the compound boils at 27° to 28° C. at 10 to 11 mm. The product thus obtained is a colourless, mobile, and easily volatile oil, very inflammable, and yielding lead oxide on burning.

The lead estimation is carried out as follows: The substance is dissolved in ten times its weight of carbon tetrachloride, cooled, and a large excess of a 10 per cent. solution of bromine in the same solvent added. The mixture is taken almost to dryness on the water-bath, then boiled a short time with a little absolute alcohol, and well cooled, the precipitate, which consists of pure lead bromide, being filtered on a Gooch crucible and washed with ice-cold alcohol.

Lead trimethyl n-propyl is prepared by the interaction of lead trimethyl chloride or bromide and magnesium n-propyl chloride, when a 90 per cent. yield is obtained. In the vacuum distillation the receiver must be cooled to at least −10° C. to avoid loss, the properties of the body being the same as the above compound.

[1] Grüttner and Krause, *Ber.*, 1916, 49, 1125.

The following bodies are obtained in a similar manner, the yields being indicated: *lead trimethyl n-butyl* (80 per cent.); *lead trimethyl isobutyl* (90 per cent.); *lead trimethyl isoamyl* (80 per cent.). Substituting lead triethyl chloride or bromide for the trimethyl compound, the following are isolated: *lead methyl triethyl* (90 per cent.); *lead triethyl n-propyl* (95 per cent.); *lead triethyl isobutyl* (92 per cent.); *lead triethyl isoamyl* (94 per cent.).

The physical constants of the compounds are shown in Table XIX. of the Appendix.

Lead tetra-alkyls containing one or two secondary radicles can easily be obtained by the action of lead alkyl mono- or dihalides on secondary magnesium alkyl halides, whilst those containing three secondary radicles are derived primarily from the tetra-alkyls.[1] Table XX. of the Appendix gives a list of these compounds, together with their physical constants.

Alkyl Derivatives of the Type R_2PbR_2'.

In the preparation of these compounds it has been found advantageous to make a paste of the lead dialkyl halides, and then add this to the Grignard reagent. The properties of the compounds are similar to those described for the lead trialkyl alkyls. The simplest member of this series, lead dimethyl diethyl, has given rise to some discussion regarding its physical constants. It was prepared by the action of magnesium methyl iodide on lead diethyl chloride. Its properties are shown below:

Grüttner and Krause:[2]

B.pt. 51° C. at 13 mm.; density, 1·7906 at 20° C.; n_D 1·5177; $n_F - n_C$ 0·01785 at 20° C.
B.pt. 54° C. at 18 mm.

Moller and Pfeiffer:[3]

B.pt. 52° C. at 14 mm.; density 1·7851 at 20° C.; n_D 1·5164; $n_F - n_C$ 0·01832 at 20° C.

Table XXI. of the Appendix gives a list of the compounds made up to the present time together with their physical constants.

Alkyl Derivatives of the Type $R_2PbR'R''$.

Halogen substitution products of lead alkyls with secondary alcoholic radicles have been isolated[4] by the reduction of ketones at a lead cathode, when a mixture of stable and unstable lead alkyls is produced. The compounds containing one or more secondary radicles are produced in the usual way from lead alkyl mono- or dihalides. Since, however, the lead atom seems less firmly attached to a secondary than a primary group, the following compounds differ from the tetra-alkyls containing normal radicles. They are unstable in air, and the secondary radicle is expelled by bromine at −75° C., even before a lighter group. If the compound contains two secondary groups, both are split off, whereas with normal radicles only one is removed at this temperature.

Compounds of the above type, together with their physical constants, are shown in Table XXII. of the Appendix.[5]

[1] Grüttner and Krause, *Ber.*, 1917, 50, 278, 574.
[2] Grüttner and Krause, *ibid.*, 1916, 49, 1546.
[3] Moller and Pfeiffer, *Ber.*, 1916, 49, 2441.
[4] Tafel, *Ber.*, 1911, 44, 334.
[5] Grüttner and Krause, *Ber.*, 1917, 50, 202, 574.

Alkyl Derivatives of the Type RR'R''R'''Pb.[1]

Lead methyl ethyl n-propyl n-butyl.—Lead dimethyl ethyl n-propyl is brominated at −75° C., when one methyl group is split off and the bromide formed. The latter is then treated with n-butyl magnesium bromide, the above compound being obtained in 90 per cent. yield. It has B.pt. 103° C. at 13 mm.; density 1·5068 at 23·5° C.; n_D 1·5072; $n_F - n_C$ 0·01607 at 22·4° C.

Lead methyl ethyl n-propyl isoamyl is prepared from the bromination product of lead diethyl propyl isoamyl and methyl magnesium chloride in 85 per cent. yield. It boils at 115° C. at 15 mm.; density 1·4792 at 21° C.; $n_{H\alpha}$ 1·50189; n_D 1·50636; $n_{H\beta}$ 1·51747; $n_{H\gamma}$ 1·52720 at 21° C.

Lead ethyl n-propyl n-butyl isoamyl is obtained in 75 per cent. yield by treating the bromination product of lead methyl ethyl n-propyl n-butyl with isoamyl magnesium chloride. It boils at 144° C. at 14 mm.; density, 1·3699 at 23·3° C.; n_D 1·5028 at 21·5° C.; $n_F - n_C$ 0·01473.

Alkyl Derivatives of the Type R_3PbX.

Lead trimethyl chloride, $Pb(CH_3)_3Cl$.[2]—When hydrochloric acid reacts with lead tetramethyl, one methyl group is displaced, and the solution on cooling deposits glistening needles of the above compound. If the substance be recrystallised from water it appears in prisms. The body is somewhat soluble in boiling alcohol, and can be sublimed. It has been more recently prepared [3] by the chlorination of lead tetramethyl at −60° C. in ethyl acetate solution. It is stated to be the most difficultly soluble of all the lead trialkyl halides, but easily soluble in ethyl acetate, and insoluble in light petroleum. It gradually sublimes at 187° C., but more rapidly at 195° C. *Lead trimethyl bromide* is prepared by similar methods to the chloride, and forms white prisms from ethyl acetate, which sinter at 131° C. *Lead trimethyl iodide* is formed by the interaction of lead tetramethyl and iodine. It crystallises in colourless needles from alcohol, is sparingly soluble in water, and sublimes unchanged on heating. When the iodide is distilled with caustic alkali, *lead trimethyl hydroxide* is formed. The *fluoride* crystallises in needles, density 3·53 at 16° C., which explode feebly about 305° C.[4]

Lead triethyl chloride, prepared in the usual way, forms white needles, M.pt. 172° C.[5] The compound is easily soluble in alcohol and ether. The *bromide* crystallises from ether in needles, M.pt. 103° to 104° C.; but the *iodide* is an oil, and has not been obtained in a pure state.[6]

Lead triethyl hydroxide may be obtained from the chloride by means of alcoholic potassium hydroxide; it is strongly alkaline, difficultly soluble in water, and readily forms salts. Löwig isolated the *sulphate*,

[1] Grüttner and Krause, *Ber.*, 1917, 50, 209.
[2] Cahours, *Annalen*, 1862, 122, 48.
[3] Grüttner and Krause, *Ber.*, 1916, 49, 1415.
[4] Krause and Pohland, *Ber.*, 1922, 55, [B], 1282.
[5] Buckton, *Annalen*, 1859, 112, 227; Pfeiffer and Truskier, *Ber.*, 1904, 37, 1125; Grüttner and Krause, *loc. cit.*; Cahours, *loc. cit.*
[6] Löwig, *Annalen*, 1853, 88, 318; Klippel, *Jahresber.*, 1860, p. 381; *J. prakt. Chem.*, 1860, [I], 81, 286.

which crystallises in octahedra, insoluble in water, alcohol, or ether, and the *nitrate*, which is easily soluble in alcohol or ether. The following derivatives are also known: the *carbonate*, a crystalline powder, insoluble in water, with difficulty in alcohol or ether; the *thiocyanate*, which crystallises from ether, soluble in water or alcohol; the *cyanide*, prisms from ether, insoluble in water, soluble in alcohol, decomposing with explosion and separation of metallic lead when heated; the *phosphate*, soluble in the above solvents; the *formate*, *acetate*, *butyrate*, *oxalate*, and *ditartrate*, all of which are easily soluble in water, alcohol, or ether. *Two double salts* of lead triethyl chloride are also known, $PbEt_3Cl.HgCl_2$ and $2PbEt_3Cl.PtCl_4$, the latter being difficultly soluble in water, but easily in alcohol or ether. The *fluoride* crystallises in prisms, density 2·48 at 16° C., decomposing about 240° C.

Lead tri-n-propyl chloride.[1]—Twenty grams of n-propyl iodide in dry ether are treated with 2·7 grams of magnesium, and after the latter has dissolved, 2 grams of lead chloride are added in small portions, and the mixture boiled for two hours. After decomposition with water the ether layer is separated off, and dried over calcium chloride. Into the well-cooled ether solution, which now contains lead tetra-n-propyl, dry hydrogen chloride is passed, until a precipitate begins to appear. The ether is then separated off, and the residue dissolved in alcohol, and after taking this to dryness the residue is crystallised from alcohol or ligroin, when flat, colourless needles are obtained, M.pt. 137° C. The compound is sparingly soluble in water, more soluble in alcohol, ether, chloroform, benzene, or ligroin. It does not combine with pyridine, but when shaken with moist silver oxide, *lead tri-n-propyl hydroxide* is obtained. The latter compound absorbs carbon dioxide from the air, and yields salts with acids. With hydrogen bromide the *bromide* is obtained, which crystallises in needles, M.pt. 82° C., and has the same solubility as the chloride. The *sulphate*, from sulphuric acid and the hydroxide, is easily soluble in water, but insoluble in the usual organic solvents. Its solution in concentrated sulphuric acid soon becomes turbid, at the same time emitting numerous small bubbles. The compound decomposes when heated, before melting. The *acetate* crystallises in colourless needles, M.pt. 116° C., soluble in the usual organic solvents. The *fluoride* crystallises in bushy needles, density 1·56 at 18° C., exploding at about 235° C.

Lead tri-n-butyl chloride is obtained from magnesium butyl iodide, and lead chloride, the product being treated with hydrogen chloride as above. It forms colourless, flat needles which melt to a clear liquid at 109° to 110° C., and have a similar solubility to the propyl compound. The *hydroxide* is prepared by dissolving the chloride in aqueous alcohol and shaking with silver oxide. The solution in water has an alkaline reaction, and absorbs carbon dioxide from the air. When treated with hydrogen bromide a white precipitate of *lead tri-n-butyl bromide* separates, which may be recrystallised from ether or chloroform.

Lead tri-isobutyl chloride[2] melts at 122° C. without decomposition; the *bromide* has M.pt. 107° to 108° C.; the *iodide* forms yellow plates, which decompose when heated; the *fluoride* forms prisms, decomposing at about 230° C. and having a density of 1·50 at 17° C.

[1] Pfeiffer, Truskier, and Disselkamp, *Ber.*, 1916, 49, 2445.
[2] Grüttner and Krause, *Ber.*, 1917, 50, 278.

Lead tri-isoamyl chloride.[1]—This compound is stated to be crystalline, but no melting-point is given. The *bromide* sinters at 129° C. and melts at 132° to 133° C.; the *iodide*, which was originally obtained by heating sodium-lead alloy with isoamyl iodide, and treating the reaction product with iodine, crystallises in yellow plates, which are insoluble in water, and with difficulty in alcohol or ether. It forms an addition product with mercuric iodide, $Pb(C_5H_{11})_3I.HgI_2$. The free base, *lead tri-isoamyl hydroxide*, is prepared from the iodide by means of silver oxide. The *fluoride* forms long, colourless needles, density 1·46 at 17° C., decomposing at about 251° C.

Alkyl Derivatives of the Type R_2PbX_2.

Lead dimethyl dichloride,[2] $Pb(CH_3)_2Cl_2$.—When lead tetra-alkyls are treated with halogen at −20° C. two alkyl groups are removed. The dichloride is practically insoluble in most organic solvents, and has a strong acid reaction in warm water. The *oxide* dissolves in weak acids and in caustic alkalies. The *sulphide* is soluble in hydrochloric acid or ammonium sulphide, insoluble in acetic acid, but the *chromate* is soluble in the latter. The *dibromide* has similar properties to the dichloride, and a *di-iodide* has also been prepared.

Lead diethyl dichloride may be prepared as above or from lead diethyl diphenyl by the action of hydrochloric acid or by thallic chloride.[3] It crystallises from alcohol in pale yellow needles. The corresponding *dibromide* is prepared from lead diethyl diphenyl by the action of dry hydrogen bromide. It crystallises in glistening, yellow prisms, which become white on long standing in air, and are decomposed by hot solvents.

Lead di-n-propyl dichloride is more stable than most of the lead dialkyl dichlorides. In contact with water or alcohol at 30° C. it slowly splits off lead chloride, and when heated to 228° C. it decomposes.

Lead di-isobutyl dichloride crystallises in white plates from hot alcohol, and the *dibromide* melts at 102° to 103° C. with decomposition.

Lead di-isoamyl dichloride decomposes at 108° C., and the *dibromide* sinters at 93° C.

Alkyl Derivative of the Type $R_2PbX'X''$.

Lead di-isobutyl chlorobromide melts with sudden decomposition at 110° C.

Alkyl Derivatives of the Type $RR'PbX_2$.[4]

Lead methyl ethyl dichloride.—Twenty grams of lead trimethyl ethyl in 100 c.c. of ethyl acetate are chlorinated at −75° C., whereby the monochloride is obtained. This on chlorination without cooling yields the dichloride in quantitative yield. It is fairly soluble in warm water and alcohol and crystallises on cooling in hair-fine needles, which are not so well formed as those of lead dimethyl or diethyl dichlorides.

[1] Klippel, *Jahresber.*, 1860, p. 381; Grüttnor and Krause, *Ber.*, 1917, 50, 278.
[2] Grüttner and Krause, *Ber.*, 1916, 49, 1415.
[3] Moller and Pfeiffer, *Ber.*, 1916, 49, 2441; Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 482.
[4] Grüttner and Krause, *Ber.*, 1917, 50, 209.

In pyridine or dimethylaniline it dissolves with extraordinary ease, and heat is evolved. The pyridine addition product crystallises from alcohol in centimetre needles, but lead chloride separates on keeping. The aqueous solution of lead methyl ethyl dichloride has a feeble acid reaction, and the compound is easily soluble in potassium hydroxide, sparingly in ammonium hydroxide. Hydrogen or ammonium sulphides, from neutral, feebly alkaline, or very dilute acetic acid solutions, precipitate a white *sulphide*, soluble in hydrochloric acid or excess of ammonium sulphide. Potassium iodide solution gives a canary yellow *di-iodide*, insoluble in acetic acid, easily soluble in hydrochloric acid. With potassium chromate a bright yellow *chromate* is formed, easily soluble in acetic acid.

Lead ethyl isoamyl dichloride is obtained in quantitative yield by chlorination of lead diethyl isoamyl chloride. It crystallises in plates, sparingly soluble in water, insoluble in ether, ethyl acetate, or benzene.

Lead n-propyl isobutyl dichloride occurs in shining plates.

Lead n-propyl isoamyl dichloride is obtained from lead methyl n-propyl isoamyl chloride, and crystallises from hot alcohol, in which it is easily soluble, in plates, insoluble in benzene, ether, ethyl acetate, or water. The *sulphide* may be obtained in the usual way, and it is readily soluble in alcoholic ammonium sulphide, sparingly in aqueous ammonium sulphide.

Lead ethyl isobutyl dibromide forms a snow-white, fine powder, soluble in small quantities in warm alcohol.

Lead n-propyl isobutyl dibromide crystallises from ether in glistening plates. The *sulphide* is pale yellow.

Lead isobutyl isoamyl dibromide forms plates, M.pt. 95° C.

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Alkyl Derivatives of the Type R_3Pb.[1]

Lead triethyl, Et_3Pb.—Sixty-five grams of lead triethyl chloride, covered with 100 c.c. of distilled water, are treated with 40 c.c. of 5-Normal sodium hydroxide and the mixture stirred until solution is complete. Addition of 200 c.c. of 5-Normal sodium hydroxide precipitates the lead triethyl hydroxide, which is separated. Sixty grams of the latter in 200 c.c. of 95 per cent. alcohol are electrolysed with lead electrodes, using a current density of 0·01 amperes per sq. cm. Lead triethyl forms as an oil at the cathode. It is pale yellow in colour, density 1·94, and readily oxidised in air, giving a yellowish powder. It may be distilled in steam, and at 2 mm. pressure it boils at 100° C., but it decomposes when distilled at ordinary pressure. It is still liquid at −80° C. In dilute solution it corresponds to the simple formula, Et_3Pb, but at higher concentrations exists as Et_6Pb_2, this property being similar to that of the corresponding aryl compounds.

Aryl Derivatives of the Type R_4Pb.

Lead tetraphenyl, $Pb(C_6H_5)_4$.—This body was first prepared[2] from sodium-lead alloy, bromobenzene, and ethyl acetate by heating the mixture to boiling in an oil-bath for sixty hours. It is much more

[1] Midgley, Hoolwalt, and Calingaërt, *J. Amer. Chem. Soc.*, 1923, 45, 1821.
[2] Polis, *Ber.*, 1887, 20, 716.

readily obtained by use of the Grignard reagent,[1] the course of the reaction being represented as follows :—

$$2PbCl_2 + 4C_6H_5MgBr = Pb + Pb(C_6H_5)_4 + 4MgClBr$$

The following method of conducting the experiment is said to give a 50 per cent. yield.[2] To the Grignard solution from 12·15 grams of magnesium, 78·5 grams of bromobenzene and 200 c.c. of anhydrous ether, 400 c.c. of dry benzene are added, and 63 grams of finely divided lead chloride in one lot. After boiling for eight hours, the whole is poured into hydrochloric acid containing ice, and then filtered. The solid lead tetraphenyl, etc., is boiled with 300 c.c. of benzene for a few minutes and then filtered, the cool filtrate yielding a crop of pure lead tetraphenyl. The crystals are removed and the filtrate used to make three further extractions of lead tetraphenyl. The benzene extraction liquor is then added to the ether-benzene layer which forms the filtrate when the Grignard reaction mixture is hydrolysed and filtered. Evaporation of these solvents yields 6 to 10 grams of lead tetraphenyl. The total yield is about 29 grams.

Lead tetraphenyl crystallises in small, white needles, M.pt. 224° to 225° C., which distil unchanged at about 240° C.[3]

The body shows decomposition if heated above 270° C.[4] and burns in air with a reddish flame and the separation of lead oxide. It is moderately soluble in chloroform, benzene, or carbon bisulphide when hot, and difficultly soluble in alcohol, ether, ligroin, or acetic acid. If heated in a sealed tube with hydrochloric acid decomposition occurs, lead tetrachloride and benzene being produced. By the action of halogens or concentrated nitric acid two phenyl groups are split off, and a lead diphenyl dihalide or dinitrate formed. A similar action takes place with iodic acid, formic, acetic, trichloracetic, propionic, valeric, and p-nitrobenzoic acids.[5] With metallic chlorides the following derivatives are formed: arsenic trichloride ⟶ lead diphenyl dichloride and diphenyl arsenious chloride; antimony trichloride ⟶ lead diphenyl dichloride and diphenylstibine chloride; antimony pentachloride ⟶ lead diphenyl dichloride and diphenylstibine trichloride; bismuth tribromide ⟶ lead diphenyl dichloride and diphenylchlorobismuthine; thallic chloride ⟶ lead diphenyl dichloride and thallium diphenyl chloride;[6] tellurium tetrachloride ⟶ lead diphenyl dichloride and tellurium diphenyl dichloride.

Lead tetraphenyl[7] crystals have been shown to belong to the tetragonal system, the axial ratio, a : c = 1 : 0·3808, the corresponding tin compound giving a : c = 1 : 0·38935, and silicon tetraphenyl, a : c = 1 : 0·43969, the three compounds being isomorphous, the value of the principal axis decreasing with increase in atomic weight of the grouping element.

Lead tetra-p-tolyl may be prepared by heating under reflux 120 grams of p-bromotoluene, 300 grams of sodium-lead amalgam, 40 grams of toluene, and 4 c.c. of ethyl acetate for fifty hours in an oil-bath.

[1] Pfeiffer and Truskier, *Ber.*, 1904, 37, 1125.
[2] Gilman and Robinson, *J. Amer. Chem. Soc.*, 1927, 49, 2315.
[3] Zechmeister and Csabay, *Ber.*, 1927, 60, [B], 1617.
[4] Polis, *Ber.*, 1887, 20, 716.
[5] Goddard, Ashley, and Evans, *Trans. Chem. Soc.*, 1922, 121, 978.
[6] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 256.
[7] Polis, *loc. cit.*

After subjecting this mixture to vacuum distillation the residue is extracted with hot benzene, the solution on cooling depositing white needles, from which the ditolyl can be removed by treatment with alcohol. The colourless needles of the pure compound melt at 239° to 240° C. to a liquid which decomposes at 254° C. It is more easily soluble than the corresponding phenyl compound in benzene, carbon bisulphide, or chloroform, and is difficultly soluble in boiling alcohol. *Lead tetrabenzyl* is not obtained by this reaction.

Lead tetracyclohexyl, $Pb(C_6H_{11})_4$.[1]—To a solution of 23 grams of magnesium cyclohexyl bromide in 100 grams of ether, 10 grams of dried lead chloride are added, the reaction going smoothly, and finely divided lead separating out. After six hours' boiling the mixture is decomposed by very dilute hydrochloric acid, the ether removed, and the residue triturated with absolute alcohol, quickly dried, and crystallised from benzene. The compound separates in canary yellow plates, which slowly decompose with separation of lead at 200° C., and if rapidly heated to 225° C. explode.[2]

Lead tetra-p-xylyl, $Pb[(CH_3)_2C_6H_3]_4$.—This is isolated by treating the magnesium compound from p-bromoxylene (0·04 mol.) with tri-p-xylyl lead bromide (0·01 mol.). The compound melts to a clear liquid at 255° C., but at 270° C. decomposes with the separation of metallic lead. It crystallises from benzene in plates, and is easily soluble in chloroform, with difficulty in ether, and insoluble in alcohol.[3]

Lead tetra-α-thienyl is prepared in the same way as the corresponding tin compound. It melts at 154·5° C. (corr.).[4]

DropBooks

Aryl Derivatives of the Type R_3PbR'.

The general method of preparation of these bodies is as follows: Fifty grams of lead triphenyl bromide is added in small quantities, with continual shaking, to an ice-cooled solution of one and a half times the calculated quantity of magnesium aryl bromide, in 400 c.c. of ether. When the reaction ceases the product is boiled for one to two hours under reflux, then cooled and decomposed with aqueous ammonium chloride solution. The ether layer is separated off, dried, and after evaporation the residue is recrystallised from alcohol or alcohol-ether.[5]

Lead triphenyl p-tolyl forms hair-fine needles, M.pt. 125·5° C., decomposing about 260° C.

Lead triphenyl p-xylyl, $Pb(C_6H_5)_3.C_8H_9$, crystallises from dilute alcohol in needles, M.pt. 125·5° C. It is easily soluble in ether, benzene, or chloroform, slightly so in cold alcohol, more readily in hot alcohol.

Lead triphenyl m-xylyl crystallises from alcohol in star-like groups of rod-shaped crystals, M.pt. 111·5° to 112° C.

Lead triphenyl p-phenetyl crystallises from alcohol in fine, white needles, M.pt. 119° to 120° C.

[1] Grüttner, *Ber.*, 1914, 47, 3257.

[2] This body has also been obtained by the interaction of lead tricyclohexyl bromide and magnesium cyclohexyl bromide (Krause, *Ber.*, 1921, 54, [B], 2066). Krause states that his preparation became yellow at 130° C., and blackened at 160°, and it crystallised in colourless, rectangular plates, easily soluble in hot benzene, sparingly in alcohol.

[3] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2165.

[4] Krause and Renwanz, *Ber.*, 1927, 60, [B], 1582.

[5] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2150.

Lead triphenyl cyclohexyl, $Pb(C_6H_5)_3.C_6H_{11}$, forms flat lancets, M.pt. 119° C.

Lead triphenyl α-naphthyl crystallises from hot alcohol in characteristic flat, yellow, warty tufts of needles, M.pt. 101° C., which are easily soluble in ether, benzene, or chloroform.

Lead triphenyl p-phenoxyphenyl forms microscopic white crystals, melting at 127° C. and decomposing at 260° C.[1]

Aryl Derivatives of the Type $R_2PbR'_2$.

Lead diphenyl di-α-naphthyl, $Pb(C_6H_5)_2(C_{10}H_7)_2$.—This is obtained as a snow-white, granular, crystalline powder by the interaction of lead diphenyl dibromide and magnesium α-naphthyl bromide. The product melts at 197° C., lead separating at a higher temperature, and it is soluble in ether, benzene, or hot alcohol. It reacts with thallic chloride according to the equation:[2]

$$Pb(C_6H_5)_2(C_{10}H_7)_2+TlCl_3=Pb(C_6H_5)_2Cl_2+Tl(C_{10}H_7)_2Cl$$

Lead diphenyl di-o-tolyl.[3]—To a solution of 5·6 grams of o-bromotoluene and 0·8 gram of magnesium in dry ether, 5 grams of lead diphenyl iodide are slowly added. After the reaction has subsided, the mixture is heated for half an hour on the water-bath, cooled, and 25 c.c. of toluene added, the whole then being decomposed with dilute hydrochloric acid. The toluene-ether layer is separated, the solvents removed, and the residue subjected to steam distillation to remove the last traces of toluene. An oil is obtained which soon solidifies to a yellow mass; this when crystallised from alcohol appears as white needles, sintering at 129° C., and melting at 134° to 135° C. It is readily soluble in cold chloroform and in hydrocarbons.

Lead diphenyl dicyclohexyl may be prepared either by the interaction of magnesium cyclohexyl bromide and lead diphenyl dibromide or magnesium phenyl bromide and lead dicyclohexyl dibromide. It forms pale yellow needles, M.pt. 178° to 180° C., the yellow liquid soon depositing metallic lead. The compound is soluble in alcohol, benzene, carbon tetrachloride, or ethyl acetate.[4]

Lead diphenyl di-p-xylyl forms colourless, prismatic rods, M.pt. 94° C., decomposing at about 250° C., easily soluble in benzene, chloroform, or ether, sparingly in cold alcohol.[5]

Aryl Derivatives of the Type Alk_3PbAr.

The general equation for the preparation of this type of compound is as follows:—[6]

$$Alk_3Pb.Hal+Ar.Mg.Hal=Alk_3PbAr.+Mg.Hal_2$$

The lead trialkyl aryls are colourless, oily, strongly refracting liquids, having a faint, characteristic odour. They are insoluble in water, but

[1] Krause and Schlöttig, *Ber.*, 1925, 58, [B], 427.
[2] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 485.
[3] Lederer, *Ber.*, 1916, 49, 349.
[4] Grüttner, *Ber.*, 1914, 47, 3257.
[5] Krause and Schlöttig, *loc. cit.*
[6] Grüttner and Grüttner, *Ber.*, 1918, 51, 1293.

miscible with the usual organic solvents. Under a pressure of 13 to 16 mm. they boil without decomposition in a carbon dioxide atmosphere, the only exception being lead triethyl benzyl, which shows a separation of dibenzyl. The compounds decompose at 200° C. with separation of lead and feeble explosion, burning with a reddish flame, and giving lead oxide. The trimethyl compounds are volatile in steam, and all the derivatives when treated with bromine in ethereal solution at —75° C. split off an alkyl or aryl group.

The crude products are obtained from 0·2 mol. of lead trialkyl bromide, and 0·3 mol. of ethereal magnesium aryl halide, the mixture being boiled for several hours under reflux, then decomposed with water, the ethereal layer washed with 10 per cent. alkali, then sulphuric acid, and the ether distilled off. The bromination of these compounds at —75° C. is carried out by adding to an ethereal solution of the lead compound, a solution of bromine in the same solvent, until the colour of the bromine persists. Aryl bromide and lead trialkyl bromide result. In the case of lead triethyl benzyl, both an alkyl and a benzyl group are split off, this being analogous to the action of bromine on lead alkyls containing a secondary alkyl group. A list of these compounds is given in Table XXIII. of the Appendix.

Aryl Derivatives of the Type Alk_2PbAr_2.

Lead diethyl diphenyl.[1]—To the solution from 15 grams of ethyl bromide and 3 grams of magnesium in 200 c.c. of dry ether, 11 grams of lead diphenyl bromide (obtained by the action of bromine on lead tetraphenyl) are added, the mixture being well shaken. The whole is boiled for an hour, cooled in ice, and decomposed with dilute hydrochloric acid. The ethereal layer is dried over calcium chloride, the ether evaporated off, and the residue distilled *in vacuo* at 20 mm. It is a colourless, very strongly refractive liquid, which shows partial decomposition when distilled, metallic lead separating out. Yield about 5 grams.

DropBooks

When treated with hydrochloric acid or chlorine, two phenyl groups are split off, and with thallic chloride it reacts as follows :—

$$Pb(C_2H_5)_2(C_6H_5)_2+TlCl_3=Pb(C_2H_5)_2Cl_2+Tl(C_6H_5)_2Cl$$

The specimen of lead diethyl diphenyl used in this reaction distilled at 182° C. at 16 mm.[2]

Lead diethyl di-α-naphthyl[3] crystallises from alcohol in white prisms, M.pt. 116° C., fairly soluble in ether.

Aryl Derivatives of the Type R_3PbX.[4]

Lead triphenyl chloride.—When the precipitate obtained by shaking lead triphenyl iodide with alcoholic caustic alkali is treated with 50 per cent. aqueous hydrochloric acid, a quantitative yield of the above chloride is produced. This crystallises from alcohol in snow-white needles, which sinter at 204° C. and melt at 206° C. It has the same solubility as the bromide.

[1] Moller and Pfeiffer, *Ber.*, 1916, 49, 2441.
[2] Goddard and Goddard, *Trans. Chem. Soc.*, 1922, 121, 483.
[3] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2150.
[4] Grüttner, *Ber.*, 1918, 51, 1298; Krause and Schmitz, *loc. cit.*

Lead triphenyl bromide.—To a solution of 51·4 grams (0·1 mol.) of finely powdered lead tetraphenyl in one litre of pyridine, cooled to −50° C. by solid carbon dioxide, a similarly cooled solution of 0·2 mol. of bromine in 200 c.c. of pyridine is added, without rise of temperature. An orange-coloured product which at first appears, gradually dissolves, and after an hour the whole is allowed to rise to room temperature and stirred. After filtering off the residue the solution is concentrated at 110° C. at 16 mm., a nearly colourless mass being obtained. This is triturated with 100 c.c. of methyl alcohol, 100 c.c. of 10 per cent. hydrobromic acid added, the whole filtered, and washed free from acid by water. After further treatment with methyl alcohol the product is practically pure, the yield being 90 per cent. of the theoretical. The compound crystallises from methyl alcohol in white, silky needles, sintering at 164° C. and melting to a clear liquid at 166° C., the latter slowly becoming turbid and lead bromide separating out. It is somewhat soluble in hot ethyl alcohol, ether, or benzene, with difficulty in cold methyl alcohol or benzene, and insoluble in water. It dissolves in alcoholic sodium or potassium hydroxide, without forming a hydroxide. When rapidly heated it explodes, emitting a reddish light and depositing metallic lead. In the dry state it does not affect the mucous membrane of the nose to the same extent as the lead alkyl halides.

Lead triphenyl iodide.[1]—If the mother-liquors of the above bromide be treated with potassium iodide, and the product obtained crystallised from water, the iodide separates in pale yellow prisms, which sinter at 139° C. and melt sharply at 142° C. to a canary yellow liquid, which soon deposits lead iodide. It is difficultly soluble in hot methyl alcohol, and insoluble in water, and is distinguished from all the other lead aryl or alkyl iodides by its stability. It does not appear to yield an oxide with alcoholic sodium or potassium hydroxide, but a white precipitate is thrown down, this yielding lead triphenyl chloride with 50 per cent. hydrochloric acid.

Lead triphenyl fluoride forms fine needles, decomposing about 318° C.; density 1·82 at 16·5° C.

Lead triphenyl sulphide is obtained as a white, flocculent precipitate by passing hydrogen sulphide into a concentrated alcoholic solution of the chloride. When freshly made it is remarkably soluble in organic solvents, and stable on heating. It is easily soluble in alcohol or ammonium sulphide, but not appreciably in water.

Lead tri-p-tolyl fluoride.[2]—A solution of the corresponding iodide is mixed with an aqueous alcoholic solution of neutral potassium fluoride, the fluoride being precipitated as a micro-crystalline powder. It crystallises from much hot alcohol in hair-like needles, decomposing at about 280° C.

Lead tri-p-tolyl iodide[3] is obtained by the action of iodine on lead tri-p-tolyl. It crystallises in pale yellow, prismatic spears, 2 to 3 cm. long, melting at 115° C. to a clear yellow liquid, which decomposes at about 195° C. with separation of lead iodide.

Lead tri-p-xylyl chloride.—Lead tri-p-xylyl is changed to the bromide, and this with potassium hydroxide yields the hydroxide, which is then treated with dilute hydrochloric acid. The chloride crystallises

[1] See Krause and Reissaus, *Ber.*, 1922, 55, [B], 897.
[2] Krause and Pohland, *Ber.*, 1922, 55, [B], 1288.
[3] Krause and Reissaus, *loc. cit.*

from alcohol in large, colourless, silvery, rectangular plates, M.pt. 167·5° C., decomposing about 195° C.

Lead tri-p-xylyl bromide.[1]—When lead tri-p-xylyl is brominated in pyridine solution at —70° C., simple addition of the halogen occurs. The compound crystallises from hot alcohol in silvery, glistening plates, M.pt. 177° C., to a clear liquid. It is easily soluble in benzene, chloroform, or hot alcohol. (It should be noted that bromination of lead tri-p-xylyl in chloroform solution at —10° C. yields lead di-p-xylyl dibromide.)

Lead tricyclohexyl fluoride is obtained from the hydroxide by the action of hydrofluoric acid or from the iodide by neutral potassium fluoride. From hot alcohol small lancets are deposited, which decompose at about 198° C. Its density at 16·5° C. is 1·79.

Lead tricyclohexyl chloride.[2]—The hydroxide is treated with dilute hydrochloric acid and the product recrystallised from hot alcohol. It forms pale yellow, hair-like needles, decomposing at 236° C.

The *bromide* may be obtained in a similar manner or by direct bromination of lead tricyclohexyl in chloroform solution at —10° C. It crystallises in yellow needles, decomposing at 210° C.

The *iodide* forms glistening, golden yellow, thick prisms, a centimetre in length. It melts at 91·7° C. and decomposes at 125° C. It is very soluble in benzene or chloroform, fairly soluble in ether or hot alcohol, sparingly in cold alcohol. When shaken in benzene solution with 30 per cent. potassium hydroxide it yields the *hydroxide*, a white, amorphous powder which has not been isolated in a crystalline form.

Aryl Derivatives of the Type R_2PbX_2.

DropBooks

Lead diphenyl dichloride, $(C_6H_5)_2PbCl_2$.[3]—This is obtained by passing dry chlorine into a carbon bisulphide solution of lead tetraphenyl and warming the mixture, when a white precipitate appears, which is washed with carbon bisulphide to remove chlorobenzene. It may also be prepared by heating lead tetraphenyl with the chlorides of arsenic or antimony, bismuth bromide, thallic chloride or stannic chloride in xylene solution.[4] A third method consists in treating the corresponding dinitrate with potassium chloride. Lead diphenyl dichloride is insoluble in alcohol or ether, slightly soluble in chloroform, benzene, or carbon bisulphide. It decomposes on melting, and when treated with silver nitrate the chlorine is removed, giving the dinitrate. With pyridine it forms a molecular compound $(C_6H_5)_2PbCl_2.4C_5H_5N$.[5]

Lead diphenyl dibromide.[6]—By treatment of the dinitrate with potassium bromide, the dibromide is isolated as a white powder which decomposes on heating, but does not melt, and appears to be more soluble than the di-iodide. It may also be obtained by direct bromination of lead tetraphenyl in chloroform solution. The following addition compounds have been isolated, $(C_6H_5)_2PbBr_2.4C_5H_5N$ and $(C_6H_5)_2PbBr_2.2NH_3$. The latter is formed when ammonia is passed through a U-tube

[1] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2165.
[2] Krause, *Ber.*, 1921, 54, [B], 2065.
[3] Polis, *Ber.*, 1887, 20, 3331.
[4] Goddard, Ashley, and Evans, *Trans. Chem. Soc.*, 1922, 121, 978; Goddard and Goddard, *ibid.*, 1922, 121, 256.
[5] Pfeiffer, Truskier, and Disselkamp, *Ber.*, 1916, 49, 2445.
[6] Polis, *Ber.*, 1887, 20, 716.

containing lead diphenyl dibromide, but by passing air over the compound the ammonia is split off again.

Lead diphenyl di-iodide.—Lead tetraphenyl in chloroform solution is treated with a solution of iodine in the same solvent, until a permanent colour of iodine remains. The solution on evaporation gives golden yellow needles of the iodide. The same result is obtained by the action of potassium iodide on lead diphenyl dinitrate. The compound melts at 101° to 103° C., and is easily soluble in chloroform, alcohol, or benzene. When its alcoholic solution is treated with silver nitrate, silver iodide and lead diphenyl dinitrate are formed.

Lead diphenyl dinitrate, $Pb(C_6H_5)_2(NO_3)_2,2H_2O$.—When lead tetraphenyl is added to a boiling solution of nitric acid (density 1·4), two phenyl groups are split off, and on cooling, the nitrate is deposited in small, glistening plates. These are purified by crystallisation from water containing nitric acid, the pure compound being fairly soluble in hot water or alcohol, and exploding on heating, without melting. When a hot aqueous solution of the nitrate is treated with ammonia, a white precipitate of the *basic nitrate* is thrown down, $Pb(C_6H_5)_2(OH)NO_3$. This also explodes without melting when heated, and by treating the normal nitrate with hot pyridine, and slowly cooling the solution, the following *complex* is deposited, $Pb(C_6H_5)_2(NO_3)_2.4C_5H_5N$.

Lead diphenyl iodate [1] is a crystalline powder, formed by heating together lead tetraphenyl and iodic acid in xylene solution. It is insoluble in the usual organic solvents.

Lead diphenyl oxide may either be obtained by treating lead diphenyl halides with ethyl alcoholic potassium hydroxide [2] or by adding a boiling solution of sodium hydroxide to a solution of lead diphenyl nitrate.[3] The oxide is precipitated as a white powder, which does not melt, and volatilises without decomposition. It is strongly basic in character, and is insoluble in the usual organic solvents, also in sodium and potassium hydroxide.

Basic lead diphenyl carbonate, $[(C_6H_5)_2Pb.OH]_2CO_3$.—The addition of sodium carbonate to a lead diphenyl salt solution causes the separation of this carbonate, which is a white, insoluble powder having no melting-point.

Lead diphenyl diformate is deposited in small, colourless needles from the solution obtained by boiling lead tetraphenyl and formic acid in benzene. It melts with decomposition above 200° C. If the formic acid be replaced by acetic acid, *lead diphenyl diacetate* crystallises out in white crystals, which are easily soluble in cold water or acetic acid. The compound thus obtained has the formula, $Pb(C_6H_5)_2(C_2H_3O_2)_2.2H_2O$, the water-free salt melting at 195° C. Using trichloracetic acid and xylene as a solvent, *lead diphenyl trichloracetate* [4] is obtained, which softens at 170° to 175° C. and decomposes rapidly at 210° C. without melting. It has the following constitution, $2C_{16}H_{10}O_4Cl_6Pb.C_2HO_2Cl_3$. The following salts have also been obtained: *Acid lead diphenyl propionate,* melting to a clear liquid at 168° to 169° C., this decomposing at 230° to 235° C.; *lead diphenyl divalerate,* white needles, M.pt. 168° to 170° C.; *lead diphenyl oxalate,* a white, crystalline powder, darkening at 280° C.

[1] Goddard, Ashley, and Evans, *Trans. Chem. Soc.*, 1922, 121, 978.
[2] Zechmeister and Csabay, *Ber.*, 1927, 60, [B], 1617.
[3] Polis, *Ber.*, 1887, 20, 716.
[4] Goddard, Ashley, and Evans, *loc. cit.*

and decomposing rapidly at 293° to 295° C.; *lead diphenyl di-p-nitrobenzoate*, small, pale yellow needles, darkening and melting at 256° C.

Lead diphenyl dicyanide [1] is obtained by treating the di-iodide in methyl alcohol suspension with silver cyanide. It decomposes at 245° to 255° C. and is converted by dilute nitric and hydrochloric acids into the corresponding dinitrate and dichloride.

Basic lead diphenyl cyanide, $Pb(C_6H_5)_2OH.CN$.[2]—If the nitrate is treated with a solution of potassium cyanide, this basic cyanide is precipitated as a white powder. It is insoluble in water, alcohol, or ether, and melts with decomposition.

Lead diphenyl dithiocyanate.—This salt is readily obtained by mixing together aqueous solutions of lead diphenyl acetate and ammonium thiocyanate. It is a white powder, insoluble in water and the usual organic solvents, and is decomposed by silver nitrate, silver thiocyanate being deposited. The salt decomposes at its melting-point.

Lead diphenyl sulphide.—When an aqueous acetic acid solution of the above acetate is decomposed with hydrogen sulphide, a white, flocculent precipitate of the sulphide is obtained. By extracting this with alcohol-benzene, and evaporating off the solvent, small, bright yellow crystals are deposited. It is essential that the reaction should be carried out in the cold, since the sulphide is decomposed by heat. The compound becomes brown when heated from 80° to 90° C., and at higher temperatures diphenyl is driven off, and pure lead sulphide remains. The salt is easily soluble in benzene, chloroform, or carbon bisulphide, but with difficulty in alcohol or ether.

Lead diphenyl chromate separates as a bright yellow, crystalline precipitate, when potassium dichromate is added to lead diphenyl dinitrate. It is insoluble in water or alcohol.

Lead diphenyl phosphate is isolated in the same way as the chromate, using sodium phosphate. It is a white, crystalline powder, which does not melt, and is insoluble in the usual organic solvents.

Lead di-p-tolyl dichloride.[3]—This is a white powder, prepared as the foregoing phenyl compound. It is moderately soluble in chloroform, carbon tetrachloride, or benzene; insoluble in alcohol or ether; by the action of alcoholic silver nitrate the chlorine may be removed. *Lead di-p-tolyl dibromide* is formed by the action of bromine on the tetra-tolyl compound. It decomposes on melting, and has a similar solubility to the chloride. The *di-iodide* is a yellow compound, readily soluble in carbon bisulphide.

Lead di-p-tolyl dinitrate crystallises in fine white needles, having 3 mols. of water of crystallisation. It is soluble in water, with difficulty in alcohol, and explodes on heating. When boiled with water, or when its nitric acid solution is precipitated with ammonia, a *basic nitrate* is obtained, $Pb(C_7H_7)_2(OH)NO_3$. This is a white, amorphous powder which does not melt, and feebly explodes on heating.

Lead di-p-tolyl diformate, formed by the action of formic acid on lead tetra-p-tolyl, crystallises from aqueous formic acid in shining, white needles, which decompose and blacken at 233° C. The *diacetate*, $Pb(C_7H_7)_2(C_2H_3O_2)_2.2H_2O$, which crystallises in fine needles, is not as

[1] Zechmeister and Csabay, *Ber.*, 1927, 60, [B], 1617.
[2] Polis, *Ber.*, 1887, 20, 716.
[3] Polis, *ibid.*, 1888, 21, 3424.

soluble as the corresponding phenyl compound, and the water free of salt melts without decomposition at 183·5° C.

Lead di-p-tolyl sulphide.—When hydrogen sulphide is passed into a solution of the above diacetate, the sulphide is deposited as a pale yellow precipitate. It is washed with hydrogen sulphide water, dried *in vacuo*, and recrystallised from alcohol-benzene. When heated to 90° C. it turns brown, at 98° C. it blackens, and at higher temperatures gives di-p-tolyl and lead sulphide. It is decomposed by light, and is very soluble in benzene, carbon bisulphide, or chloroform, with difficulty in alcohol or ether.

Lead di-p-tolyl chromate is precipitated as a yellow powder when potassium dichromate reacts with lead di-p-tolyl diacetate.

Lead di-p-xylyl dibromide [1] is obtained by the bromination of lead tri-p-xylyl in chloroform solution at −10° C. It crystallises from chloroform in colourless, glistening rods which are difficultly soluble in ether, and insoluble in alcohol. It melts about 120° C., decomposing with the separation of lead bromide.

Lead dicyclohexyl dichloride [2] is isolated (*a*) by passing hydrochloric acid gas into a suspension of lead tetracyclohexyl in chloroform, or (*b*) by treating the latter chloroform suspension at 0° C. with the calculated quantity of chlorine in carbon tetrachloride. It forms pale yellow needles, which become reddish brown at 150° C. and decompose with the deposition of lead at 180° C.

The corresponding *dibromide* is prepared (*a*) by the bromination of the tetracyclohexyl compound, or (*b*) by passing hydrobromic acid gas into a benzene solution of the tetra-compound. It is isolated in pale yellow needles, which become orange at 100° C., almost white at 160° C., and deposit lead suddenly at 225° C.[3] The *di-iodide* forms orange needles, which decompose at 100° C. and are readily soluble in hot benzene, with difficulty in hot alcohol. It may also be prepared by treating lead tricyclohexyl iodide with a solution of iodine in benzene.[4]

Lead dicyclohexyl sulphide.[5]—(1) When hydrogen sulphide is passed into a pyridine solution of the chloride or bromide (not the iodide), addition of alcohol precipitates the sulphide. (2) By passing hydrogen sulphide into a pyridine solution of lead tetracyclohexyl, kept at −10° C., the sulphide is also precipitated. The compound is washed with ice-cold alcohol, and dried *in vacuo* over phosphorus pentoxide. It is a pale yellow powder which crystallises from dilute pyridine in microscopic plates, these blackening without melting slightly above 100° C.

The action of nitric acid on lead tetracyclohexyl does not lead to the production of the corresponding nitrate, but gives lead nitrate. Silver nitrate on lead dicyclohexyl dihalides yields silver halide, and a reddish-brown precipitate which contains silver, and is probably a silver derivative of cyclohexane.

Aryl Derivatives of the Types R_2Pb. *and* R_3Pb.

Lead diphenyl.[6]—The preparation is carried out in a wide-necked, round-bottomed Jena flask, fitted with a stopper containing five holes,

[1] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2165.
[2] Grüttner, *Ber.*, 1914, 48, 3257.
[3] Krause gives the decomposition point about 142° C.
[4] Krause, *Ber.*, 1921, 54, [B], 2065.
[5] Grüttner, *loc. cit.*
[6] Krause and Reissaus, *Ber.*, 1922, [B], 55, 888.

used as follows: (1) For carrying stirrer. (2) For introducing lead chloride and magnesium compound. (3) For passing in nitrogen. (4) For thermometer. (5) For condenser.

Into this apparatus the magnesium compound from 50 grams of bromobenzene in 400 c.c. of ether is introduced, and the whole cooled in ice. With vigorous stirring and in a nitrogen atmosphere, 44 grams of lead chloride are added during three-quarters of an hour, in portions of not more than 0·3 gram, the temperature being maintained at +2° C. The ethereal solution becomes reddish brown, and the stirring is maintained for two hours, the temperature being kept at 0° C. The mass is then decomposed by small pieces of ice, and shaken with benzene in a funnel filled with nitrogen. The benzene solution is evaporated under reduced pressure in a nitrogen atmosphere to about 50 c.c. Any lead triphenyl which may have been formed crystallises out at this stage and is filtered off. When the blue-red filtrate is added dropwise to alcohol, the lead diphenyl separates out, is dissolved many times in a little benzene and fractionally precipitated by alcohol. Yield 2 to 3 grams.

The compound in the dry state is an intense bluish-red, amorphous powder, fairly soluble in benzene or ether, insoluble in alcohol. Its benzene solution reduces alcoholic silver nitrate, giving a deep black precipitate of silver. It decomposes at about 100° C., becoming colourless; changes to pale yellow at 120° C., melts above 200° C., but does not blacken at 260° C.

A better yield is obtained if the reaction be carried out in benzene instead of ether solution.

When a benzene solution of lead diphenyl is treated with an ethereal solution of magnesium phenyl bromide and boiled for a few minutes, black metallic lead separates out. The mass is decomposed with water, the solvent layer evaporated, and the residue when treated with benzene gives a good yield of lead triphenyl.

Lead di-p-tolyl is prepared in a similar way to the phenyl compound, 30 grams of p-bromotoluene give 2 grams of product. It has the same properties and reactions as the phenyl derivative.

Lead triphenyl.—The apparatus used for this and the following experiments is the same as for lead diphenyl. To the magnesium compound from 50 grams of bromobenzene in 250 c.c. of ether, 40 grams of lead chloride, in half-gram quantities, are slowly added. The reaction is carried out in nitrogen and the mixture vigorously stirred. The ethereal solution changes through brownish red to yellow, and after the addition of the lead chloride the stirring is maintained for three hours. The mass is decomposed by small pieces of ice, the ether removed under reduced pressure, and the residue filtered and washed with water and three times with alcohol, then dried at the ordinary temperature *in vacuo* over phosphorus pentoxide. The dry product is extracted with hot benzene, from which glistening rhomboidal crystals separate, containing 1 mol. of benzene of crystallisation. It crystallises from chloroform in plates. Yield 17·5 grams, 40 per cent. It commences to decompose at 155° C. and melts at 225° C. It may be converted to lead tetraphenyl (1) by heating alone, (2) by heating its benzene solution on a boiling water-bath, (3) by heating the pyridine solution at 60° to 65° C. Its solution in benzene is converted by an aqueous alcoholic solution of iodine into lead triphenyl iodide, but with a dilute solution of iodine in

benzene, lead diphenyl di-iodide and lead iodide are formed, the former only in small quantity.

Lead tri-o-tolyl crystallises from benzene or chloroform in microscopic rhombic crystals, from which lead separates at 240° C., and at 250° C. a black liquid is obtained. It slowly decomposes alcoholic silver nitrate solutions when warmed, but has no action in the cold.

Lead tri-p-tolyl is formed by the same method as the phenyl compound. It crystallises from benzene on the addition of alcohol in six-sided plates, from chloroform in rhombohedra, containing chloroform of crystallisation, these being efflorescent in the air. It commences to decompose at 193° C. and melts at 240° C. A cooled benzene solution gives a greenish precipitate with alcoholic silver nitrate, which quickly blackens as the temperature rises, but if a very low temperature is maintained the green colour remains. When heated alone or boiled in benzene solution it yields lead tetra-p-tolyl. In contrast to lead tri-p-xylyl and lead tricyclohexyl, it is converted by bromine in freezing pyridine into lead bromide and lead tetra-p-tolyl, which points to the possible existence in pyridine solution of the equilibrium :

$$2Pb(C_7H_7)_3 \rightleftharpoons Pb(C_7H_7)_4 + Pb(C_7H_7)_2$$

When the benzene solution is treated with aqueous alcoholic iodine solution, lead tri-p-tolyl iodide is formed.

Lead tri-m-xylyl.[1]—To a solution of 20·55 grams of p-bromoxylene and 3·12 grams of magnesium in 100 c.c. of ether, 11·6 grams of lead chloride are added in small quantities, and the mixture boiled for five hours. Metallic lead soon commences to separate out and the colour of the solution changes from brownish red to green. The mixture is decomposed with water, filtered, and the dry residue extracted with benzene. Evaporation of the solvent gives 2·5 grams of a very pale yellow, crystalline powder. After crystallising from acetone, then three times from benzene, it melts sharply at 233·5° C. with the separation of metallic lead. It is soluble in chloroform or toluene, slightly soluble in acetone, light petroleum, or pyridine. Its solutions precipitate silver oxide from alcoholic silver nitrate. When its benzene solution is treated with thallic chloride it yields thallous chloride and lead di-m-xylyl dichloride.

Lead tri-p-xylyl[2] sinters at 220° C., and melts with decomposition at 225° C. It is easily soluble in hot benzene or chloroform, sparingly in cold benzene or ether, and insoluble in methyl or ethyl alcohol. Its benzene solutions when exposed to air are unchanged, but in sunlight quickly deposit a white precipitate. In the dry state the compound is stable in air. Bromination at −40° C. produces lead tri-p-xylyl bromide, but at −10° C. lead di-p-xylyl dibromide is formed.

Lead tricyclohexyl[3] crystallises in bright yellow, thin, hexagonal plates, decomposing at 195° C. It is readily affected by light, the solid substance quickly becoming brown, and the benzene solution yielding a white precipitate in diffused light or a brown precipitate in direct sunlight. The benzene solution is not stable in the dark, and it reduces alcoholic silver nitrate in the usual way. When boiled with ammonium sulphide, lead sulphide is formed. A solution of iodine in

[1] Goddard, *Trans. Chem. Soc.*, 1923, 123, 1171.
[2] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2167 ; Krause and Reissaus, *loc. cit.*
[3] Krause, *Ber.*, 1921, 54, [B], 2060.

benzene when added to a benzene solution of lead tricyclohexyl yields lead tricyclohexyl iodide.

Aryl Derivatives of the Types $Ar_2AlkPbX$; $Ar_2Ar'PbX$.

Lead diphenyl methyl bromide [1] is obtained by the bromination of lead triphenyl methyl, as an oily product, which is pressed on a porous plate and recrystallised from benzene-alcohol. It forms glistening needles, M.pt. 118° C., decomposing with frothing at 124° C.

Lead diphenyl ethyl bromide forms colourless, glistening, prismatic needles, M.pt. 119° C., decomposing with gas evolution at 130° to 135° C. It is very easily soluble in benzene or chloroform, readily in ether, sparingly in cold alcohol.

Lead diphenyl p-xylyl bromide is prepared by brominating lead diphenyl di-p-xylyl, and the crude product is best recrystallised from about 80 per cent. alcohol. It crystallises in bushy groups of plates, M.pt. 90° C., decomposing at 200° C. With phenyl magnesium bromide it yields lead triphenyl p-xylyl.

Lead diphenyl cyclohexyl bromide occurs as fine groups of prismatic needles, M.pt. 135° C., decomposing at 160° C. Phenyl magnesium bromide converts it to lead triphenyl cyclohexyl.

Aryl Derivatives of the Types Ar_3PbAlk; $Ar_2Ar'PbAlk$; $Ar.Ar'PbAlkX$.[2]

Lead triphenyl methyl is prepared from lead triphenyl bromide and an excess of methyl magnesium halide. It crystallises from benzene in rhomboidal crystals, M.pt. 60° C., becoming turbid at 220° C. and decomposing at 260° C. In benzene or chloroform it is very soluble, less soluble in ether, sparingly in cold 94 per cent. alcohol. Alcoholic silver nitrate from an alcohol solution of the lead compound precipitates yellow *silver phenyl-silver nitrate*.

Lead triphenyl ethyl, [3] obtained as above, is a solid, M.pt. 42° C., giving a colourless, highly refractive liquid; density 1·5885 at 61° C.; $n_{H\alpha}$ 1·62628 at 61° C.; $\Sigma R_{H\alpha}$ 22·29.

Lead diphenyl cyclohexyl methyl is isolated from pure lead diphenyl cyclohexyl bromide and an excess of methyl magnesium bromide. It is a liquid at ordinary temperatures, miscible with most organic solvents and aqueous alcohol. When brominated it is converted into lead phenyl cyclohexyl methyl bromide.

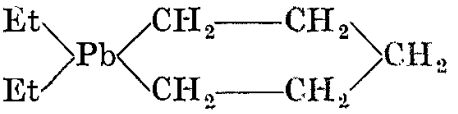
Lead phenyl cyclohexyl methyl bromide, obtained as just described, is susceptible to light and temperature. It may be crystallised from benzene, provided the temperature is kept below 70° C., small, star-shaped groups of prisms being deposited, which melt with complete decomposition at 93° to 94° C.

Heterocyclic Systems containing Lead.[4]

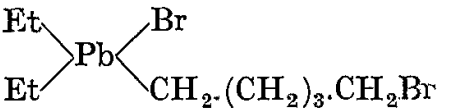
By the action of lead diethyl chloride on the magnesium compound

[1] Krause and Schlöttig, *Ber.*, 1925, 58, [B], 427.
[2] Krause and Schlöttig, *ibid.*
[3] Krause and Schmitz, *Ber.*, 1919, 52, [B], 2150.
[4] Grüttner and Krause, *Ber.*, 1916, 49, 2666.

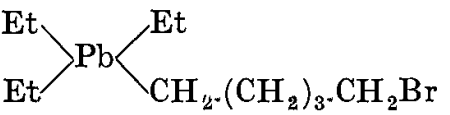
of 1 : 5-dibromopentane, lead diethyl cyclopentamethylene is obtained:



Like the tin compound, this substance is analogous to the cyclohexanes in which a carbon atom is replaced by quadrivalent lead. Molecular weight determinations point to the simple formula, $C_9H_{20}Pb$. It has previously been shown that halogens split off alkyl groups from lead tetra-alkyls, when the reaction is carried out in dilute solution at $-75°$ C. In the case of lead diethylcyclopentamethylene two possibilities occur, either a splitting off of the ethyl group and the formation of lead ethylcyclopentamethylene monohalide, or the partial scission of the ring with the formation of lead diethyl-5-halogen-amyl halide,



It is found by experiment that the reaction takes the latter course, and that the yields are quantitative. The characteristic is emphasised, that when we have a smooth addition of halogen, the splitting off of halogen hydrocarbons takes place, which is always noticed in the halogenisation of lead alkyls. In the preceding compound the carbon-bound halogen atom may be directly precipitated by silver nitrate, whilst the lead-bound halogen is not. By the action of magnesium ethyl bromide lead triethyl-5-halogen amyl is obtained:



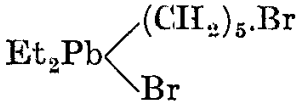
Its halogen is not directly precipitated by silver nitrate, but with magnesium powder in ethereal solution it forms the magnesium compound in 60 per cent. yield.

By the action of chlorine on lead diethylcyclopentamethylene, lead diethyl-5-chloroamyl chloride is formed, and this by the action of chlorine at low temperatures has two ethyl groups replaced by chlorine, whilst the substituted amyl group remains attached to the lead atom. This is in accordance with the observed fact that the halogen always splits off the lightest group first. The compound thus obtained, lead ethyl-5-chloroamyl dichloride, has two chlorine atoms precipitable by silver nitrate and not one. By the energetic action of chlorine on lead diethylcyclopentamethylene, lead halide, ethyl halide, and dihalogen pentane are obtained, showing that the pentamethylene ring has remained intact. The lead compound in some respects resembles the lead tetra-alkyls.

Lead diethylcyclopentamethylene, $Et_2Pb<(CH_2)_5$.—To the magnesium compound from 100 grams of 1 : 5-dibromopentane (or 65 grams of 1 : 5-dichloropentane) in 500 c.c. of ether, 50 grams of lead diethyl dichloride are added in small portions, the whole being maintained at 0° C., vigorously stirred, and a stream of nitrogen passed through. After the addition the mass is warmed on the water-bath for fifteen

minutes, decomposed with water, the ether layer removed, washed, dried, and the solvent distilled off. A colourless oil remains, and this is fractionated in a stream of hydrogen under reduced pressure. The fraction, 100° to 130° C. at 13 mm., is worked down to 109° to 114° C. at 13 mm., and this yields 40 grams of pure product, B.pt. 111° C. at 13 mm. It is a thin, colourless oil, having an odour resembling ketones. It is insoluble in water, sparingly soluble in 96 per cent. alcohol, but miscible with absolute alcohol and most organic solvents. Neutral silver nitrate is reduced in the cold, and when placed on filter paper it inflames and burns briskly, giving fumes of lead oxide. With exclusion of air it may be kept for a month, but in contact with air it is slowly oxidised, giving a brown resin.

Lead diethyl-5-bromoamyl bromide,



The above compound is brominated at −75° C. in ethereal solution, and the product fractionated after drying. It is a thick, colourless oil.

Lead triethyl-5-bromoamyl, $Et_3Pb(CH_2)_5Br$.—The preceding bromide is shaken with magnesium ethyl bromide and boiled for five minutes. Treatment in the usual manner gives an oil, B.pt. 166·8° C. at 13 mm. Yield quantitative. It is a colourless, thin oil, having an odour resembling the lead alkyls, and is completely stable in air. Treatment with magnesium powder yields *lead triethyl n-amyl*, a compound which may also be obtained from magnesium n-amyl bromide and lead triethyl bromide. Lead triethyl n-amyl is a colourless oil of faint, unpleasant smell, B.pt. 121° C. at 15 mm.

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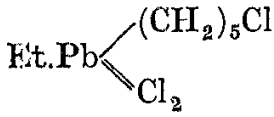
Lead ethyl-5-chloroamyl dichloride,



Lead diethylcyclopentamethylene is chlorinated at −75° C. in ethyl acetate solution. A crystalline powder is obtained which is washed with ether and recrystallised from a little alcohol. It crystallises in shining needles, insoluble in ether.

1 : 5-Bis-trimethylplumbyl-n-pentane, $Me_3Pb.(CH_2)_5.PbMe_3$.—The magnesium compound from 1 : 5-dichloropentane is caused to react with lead trimethyl bromide in ethereal solution, the reaction being completed by an hour's warming on the water-bath. The excess of lead trimethyl bromide is removed by shaking the mass with 20 per cent. potassium hydroxide and dilute sulphuric acid. The ethereal solution is then evaporated and the residual oil fractionated under reduced pressure. The pure product is a colourless oil. B.pt. 166·5° C. at 14 mm.

Table XXIV. of the Appendix shows the physical constants of the above compounds.

APPENDIX.

TABLE I.—PHYSICAL CONSTANTS OF ZINC DIALKYLS.

Compound.	Boiling-point. °C.		Density D_4 (vac.).		t^1.	Density D_4^t (vac.).	nH_α^t.	nD^t.	$nH_\beta^t - nH_\alpha^t$.	Molecular Refraction.			Atomic Refraction of Zinc.		
	$t°$.	At mm.								H_α.	D.	$H_\beta - H_\alpha$.	H_α.	D.	$H_\beta - H_\alpha$.
Zinc diethyl . .	16	9·5	8·0	1·245[2]	8	1·245	1·4936[2]	..	0·0205[2]	28·847[2]	..	1·010[2]	8·271[2]	..	0·683[2]
Zinc ethyl n-propyl	27	10	18·5	1·1558	17	1·1572	1·48511	1·48913	0·01416	34·054	34·293	0·843	8·880	9·004	0·445
Zinc di-n-propyl .	48	10	20·2	1·1034	18·6	1·1049	1·48030	1·48452	0·01399	38·967	39·259	0·965	9·196	9·352	0·497
Zinc ethyl isobutyl	48	11	16·6	1·0861	16·6	1·0861	1·47142	1·47507	0·01327	39·013	39·272	0·937	9·242	9·365	0·469
Zinc n-propyl isobutyl[3] . .	52	9	17·0	1·0465	15·9	1·0475	1·46601	1·46966	0·01269	43·759	44·053	1·020	9·391	9·529	0·480
Zinc di-isobutyl .	55	10	16·5	1·0080	16·0	1·0085	1·45698	1·46034	0·01183	48·474	48·782	1·080	9·508	9·640	0·471
Zinc isopropyl isoamyl . .	84	11	18·1	1·0058	16·0	1·0078	1·46601	1·46937	0·01162	53·187	53·517	1·135	9·623	9·757	0·455
Zinc di-isoamyl .	102	10	19·0	0·9939	17·0	0·9958	1·46690	1·47045	0·01141	57·826	58·203	1·209	9·663	9·825	0·460

[1] t=temperature at which the refractions were measured, and the next column gives the recalculated densities for this temperature.

[2] Values after Gladstone, *Trans. Chem. Soc.*, 1896, 59, 293, 296; the values for the molecular refraction, etc., were calculated from the Lorentz-Lorenz formula.

[3] For zinc n-propyl isobutyl the values for nH_γ were also made, $nH_\gamma^{15.9°}$ 1·48628, $MR_{H\gamma}$ 45·386, $AR_{H\gamma}$ 10·169.

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TABLE II.—PHYSICAL CONSTANTS OF CADMIUM DIALKYLS.

Compound.	M.pt. ° C.	B.pt. ° C.	Density (vacuum).	n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.	Molecular Weight.	
								Found.	(Calc.).
Cadmium dimethyl	—4·5	105·5/758 mm.	$D_4^{17.9}$ 1·9846	1·57766	1·58488	1·60381	1·62053 at 17·9 ° C	146	142
Cadmium diethyl .	— 21	64/19·5 ,,	$D_4^{18.1}$ 1·6564	1·56152	1·56798	1·58447	1·59887 ,, 18·1	210	170
Cadmium di-n-propyl . .	— 33	84/21 ,,	$D_4^{17.6}$ 1·4201	1·52412	1·52906	1·54267	1·55452 ,, 17·6	208	199
Cadmium di-n-butyl . .	— 48	103·5/12·5 ,,	$D_4^{19.5}$ 1·3056	1·51100	1·51546	1·52762	1·53793 ,, 19·5	235	227
Cadmium di-iso-butyl . .	— 37	90·5/20 ,,	D_4^{18} 1·2693	1·49528	1·49966	1·51160	1·52173 ,, 18·0	250	227
Cadmium di-iso-amyl . .	—115	121·5/15 ,,	D_4^{19} 1·2210	1·49967	1·50389	1·51470	1·52412 ,, 19·0	..	..

*

TABLE III.—ATOMIC REFRACTION AND DISPERSION OF CADMIUM DIALKYLS.

Compound.	ΣR_{H_α}.	ΣR_D.	$\Sigma\Delta_{\gamma-\alpha}$.	$\Sigma\Delta_{\beta-\alpha}$.	MR_{H_α}.	MR_D.	$M\Delta_{\gamma-\alpha}$.	$M\Delta_{\beta-\alpha}$.	AR_{H_α}.	AR_D.	$A\Delta_{\gamma-\alpha}$.	$A\Delta_{\beta-\alpha}$.
Cadmium dimethyl .	16·70	16·88	1·01	0·62	23·78	24·04	1·44	0·89	12·40	12·61	1·15	0·70
Cadmium diethyl .	19·57	19·75	1·06	0·66	33·36	33·68	1·81	1·12	12·78	13·00	1·30	0·79
Cadmium di-n-propyl	21·55	21·72	0·94	0·64	42·78	43·12	2·06	1·26	13·00	13·21	1·32	0·80
Cadmium di-n-butyl	22·95	23·11	1·01	0·63	51·97	52·35	2·28	1·41	13·01	13·21	1·32	0·81
Cadmium di-isoamyl	22·99	23·16	1·03	0·64	52·08	52·46	2·33	1·44	13·10	13·32	1·37	0·84
Cadmium di-isobutyl	24·07	24·25	0·99	0·61	61·27	61·71	2·52	1·55	13·11	13·33	1·33	0·80

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The deduced atomic refraction and dispersion of cadmium is as follows :—

$$AR_{H_\alpha}=13{\cdot}06\ ;\ AR_D=13{\cdot}27\ ;\ A\Delta_{\gamma-\alpha}=1{\cdot}34\ ;\ A\Delta_{\beta-\alpha}=0{\cdot}81.$$

Looking at the periodic system, cadmium has a high atomic refraction, mercury in mercury diethyl having the value $AR_{H_\alpha}=12{\cdot}81$, and zinc in zinc diethyl $AR_{H_\alpha}=8{\cdot}29$. The figures agree, however, with the higher boiling-point values.

TABLE IV.—INTERACTION OF THALLIC CHLORIDE WITH ORGANOMETALLIC COMPOUNDS.

Compounds Reacting with Thallic Chloride.	*Products of Reaction.*
Mercury di-n-propyl	n-Propylmercuric chloride, thallous chloride.
Mercury di-*isoamyl*	Isoamylmercuric chloride, thallous chloride.
Tin tetraethyl	Thallium diethyl chloride, tin diethyl dichloride.
Tin dimethyl diethyl	Thallium diethyl chloride, tin dimethyl dichloride, thallous chloride.
Tin triethyl chloride	Tin diethyl dichloride, thallous chloride, ethyl chloride.
Tin triethyl iodide	Tin diethyl dichloride, thallium, iodine, iodine monochloride.
Lead tetraethyl	Lead diethyl dichloride, thallous chloride, butane.
Lead triethyl methyl	Lead triethyl chloride, thallous chloride, methyl chloride
Lead triethyl chloride	Lead diethyl dichloride, thallous chloride, ethyl chloride.
Mercury diphenyl	Thallium diphenyl chloride, mercuric chloride.
Mercury dibenzyl	Benzylmercuric chloride, thallous chloride.
Mercury ethyl benzyl	Ethylmercuric chloride, benzylmercuric chloride, thallous chloride.
Tin tetraphenyl	Thallium diphenyl chloride, tin triphenyl chloride, tin diphenyl hydroxychloride, hydrochloric acid.
Lead tetraphenyl	Thallium diphenyl chloride, lead diphenyl dichloride.
Lead tri-m-xylyl	Lead di-m-xylyl dichloride, thallous chloride.
Lead diethyl diphenyl	Thallium diphenyl chloride, lead diethyl dichloride.
Lead diphenyl di-α-naphthyl	Thallium di-α-naphthyl chloride, lead diphenyl dichloride.
Triphenylphosphine	Triphenylphosphine, thallous chloride, chlorine.
Triphenylarsine	(*a*) In the cold. Thallous chloride, phenylarsenious dichloride. (*b*) Hot. Triphenylarsine dichloride, thallium diphenyl chloride, thallous chloride.
Tri-m-, tri-p-xylylarsine	Thallous chloride, m-xylyl and p-xylylarsenious dichlorides.
Triphenylstibine	Triphenylstibine dichloride, thallous chloride.
Tri-m-xylylstibine	Tri-m-xylylstibine dichloride, thallous chloride.
Triphenylbismuthine	Thallium diphenyl chloride, diphenylchlorobismuthine.
Tri-p-tolyl-, tri-α-naphthyl-bismuthine	Thallium di-p-tolyl chloride, di-p-tolylchlorobismuthine; thallium di-α-naphthyl chloride, di-α-naphthylchlorobismuthine.

TABLE V.—SHOWING GRADUATION IN MELTING- AND BOILING-POINTS OF COMPOUNDS FROM GROUP IV.

$SiMe_4$, B.pt. 121° to 126° C.	$GeMe_4$, B.pt 43·4° C.	$SnMe_4$, B.pt. 76° to 77° C.	$PbMe_4$, B.pt. 110° C.
$SiEt_4$, B.pt. 151° to 154° C.	$GeEt_4$, B.pt. 163·5° C.	$SnEt_4$, B.pt. 175° C.	$PbEt_4$, B.pt. 91° to 92° C./19 mm.
$SiPh_4$, M.pt. 233° to 234° C.	$GePh_4$, M.pt. 226° (230° to 231° C.).	$SnPh_4$, M.pt. 224° to 225° C.	$PbPh_4$, M.pt. 224° to 225° C.
Ph_3SiBr, M.pt. 118° to 120° C.	Ph_3GeBr, M.pt, 138° C.	Ph_3SnBr, M.pt. 120·5° C.	Ph_3PbBr, M.pt. 166° C.
Ph_2SiCl_2, B.pt. 230° to 237° C./90 mm.	..	Ph_2SnCl_2, M.pt. 42° C.	Ph_2PbCl_2, Decomp.; no M.pt.
$Ph_3Si.SiPh_3$, M.pt. 354° C.	$Ph_3Ge.GePh_3$, M.pt. 340° C.	$Ph_3Sn.SnPh_3$, M.pt. 237° C.	..
$Me_2Si<(CH_2)_5$, B.pt. 133° to 134° C./752·9 mm.	..	$Et_2Sn<(CH_2)_5$, B.pt. 95° C./14 mm.	$Et_2Pb<(CH_2)_5$, B.pt. 111° C./15 mm.
$HO(SiPh_2.O)_3SiPh_2.OH$, M.pt. 128·5° C.	$HO(GePh_2.O)_3GePh_2.OH$, M.pt. 149° C.	..	..
$O<\begin{matrix}SiPh_2.O.SiPh_2\\SiPh_2.O.SiPh_2\end{matrix}>O$, M.pt. 201° C.	$O<\begin{matrix}GePh_2.O.GePh_2\\GePh_2.O.GePh_2\end{matrix}>O$, M.pt. 218° C.	..	..
$Me.SiOOH$, No M.pt.	..	$Me.SnOOH$, No M.pt.	..
$(Ph_3Si)_2O$, M.pt. 222° C.	$(Ph_3Ge)_2O$, M.pt. 182° to 183° C.	..	..
..	..	Ph_3Sn, M.pt. 229° to 232° C.	Ph_3Pb, M.pt. 225° C.

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TABLE VI.—REFRACTIVITIES OF SOME SILICON COMPOUNDS OF THE TYPE $Alk_3Si.Ar$.

Substance.	M_{H_α}.	$_DM$.	$M_{H_\beta}-M_{H_\alpha}$.	$M_{H_\gamma}-M_{H_\alpha}$.
$(C_2H_5)_3SiC_6H_4Cl$ . .	68·35	68·82	1·628	2·628
$(C_2H_5)_3SiC_6H_4Br$ . .	71·79	72·30	1·780	2·878
$(C_2H_5)_3SiC_6H_4I$ . .	78·30	78·91	2·149	3·438
$(n\text{-}C_3H_7)_3SiC_6H_4Cl$.	82·65	83·19	1·897	3·026

By subtracting from these values the atomic equivalents of carbon, hydrogen, and halogen, the atomic refraction of the silicon in the compounds is as follows :—

Substance.	Si_{H_α}.	Si_D.	$Si_{H_\beta-H_\alpha}$.	$Si_{H_\gamma-H_\alpha}$.
$(C_2H_5)_3SiC_6H_5$ . .	7·52	7·59	0·31	0·53
$(C_2H_5)_3SiC_6H_4Cl$ . .	7·60	7·74	0·423	0·685
$(C_2H_5)_3SiC_6H_4Br$ . .	8·22	8·32	0·439	0·702
$(C_2H_5)_3SiC_6H_4I$ . .	9·78	9·89	0·537	0·949
$(n\text{-}C_3H_7)_3SiC_6H_4Cl$.	8·15	8·26	0·431	0·696

[See Bygdén, *Ber.*, 1915, **90**, 243.]

*

TABLE VIA.—PHYSICAL CONSTANTS OF SOME ORGANOSILICON COMPOUNDS.

No.	Compounds.	Boiling-point.	Density.	n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.	° C.
1	p-$Br.C_6H_4.Si(OCH_3)_3$ . . .	136° C./13·5 mm.	$D_4^{16·5}$ 1·3525 ; D_4^{20} 1·3493	1·50791	1·51210	1·52296	..	16·5
2	p-$Br.C_6H_4.Si(OC_2H_5)_3$ . . .	149–150° C./12 mm.	$D_4^{16·4}$ 1·2276 ; D_4^{20} 1·2244	1·48872	1·49247	1·50206	..	15·4
3	p-$Br.C_6H_4.Si(OC_3H_7)_3$ . . .	175–176° C./14 mm.	$D_4^{18·8}$ 1·5464 ; D_4^{20} 1·1553	1·48144	1·48497	1·49386	1·50129	16·6
4	p-$Br.C_6H_4.Si(O\text{-}i\text{-}C_4H_9)_3$ . . .	190–191° C./14 mm.	$D_4^{17·2}$ 1·0949 ; D_4^{20} 1·0923	1·47531	1·47865	1·48698	1·49424	14·9
5	$(C_2H_5)_3Si.C_6H_4.CH(OH).CH_3$ . .	173–174° C./14·5 mm.	$D_4^{19·5}$ 0·9601 ; D_4^{20} 0·9596	1·51404	1·51822	1·52885	1·53810	17·2
6	$(C_2H_5)_3Si.C_6H_4.CH(OH).CH_2.CH_3$.	185° C./16·5 mm.	$D_4^{17·0}$ 0·9603 ; D_4^{20} 0·9575	1·51243	1·51661	1·52734	..	18·0
7	$(C_2H_5)_3Si.C_6H_4.CH(OH).CH_2.CH_2.CH_3$	199–201° C./21 mm.	D_4^{14} 0·9546 ; D_4^{20} 0·9491	1·50373	1·50754	1·51737	..	..
8	$(C_2H_5)_3Si.C_6H_4.CH(OH).CH(CH_3)_2$.	190–192° C./18 mm.	$D_4^{17·5}$ 0·9535 ; D_4^{20} 0·9512	1·50820	1·51212	1·52231	..	19·2
9	$(C_2H_5)_3Si.OH$	70·5° C./16·5 mm.	$D_4^{19·7}$ 0·8650 ; D_4^{20} 0·8647	1·43393	1·43639	1·44228	1·44675	16·5
10	p-$(C_2H_5)_3Si.C_6H_4.SiCl_3$ . . .	173–176° C./13·5 mm.	.. ..	..	..	..	..	..
11	$(C_2H_5)_3Si.C_6H_4.Si(C_2H_5)_3$ . .	195–196° C./16·5 mm.	$D_4^{17·6}$ 0·8989 ; D_4^{20} 0·8967	1·50555	1·50942	1·51945	1·52788	15·7
12	$(C_2H_5)_2SiBr$	66·5° C./24 mm.	.. .. D_4^{20} 1·1766	1·46402	1·46705	1·47447	1·48074	15·7
13	$C_6H_5.p\text{-}C_6H_4.Br.SiCl_2$ . .	199–200° C./14 mm.	$D_4^{18·5}$ 1·5019 ; D_4^{20} 1·5005	1·60294	1·60921	1·62531	1·63953	19·0
14	$C_6H_5.p\text{-}C_6H_4Br.Si(OC_2H_5)_2$.	201° C./17 mm.	$D_4^{21·5}$ 1·2474 ; D_4^{20} 1·2488	1·54525	1·55031	1·56322	1·57467	19·0
15	$[C_6H_5.p\text{-}C_6H_4Br.Si(OC_2H_5)]_2O$ . .	317–318° C./20 mm.	D_4^{22} 1·3350 ; D_4^{20} 1·3369	1·57867	1·58437	1·59895	1·61146	18·6
16	$C_6H_5.p\text{-}C_6H_4Br.Si(C_2H_5)_2$ . .	203–203·5° C./13·5 mm.	$D_4^{19·7}$ 1·2156 ; D_4^{20} 1·2153	1·57794	1·58351	1·59781	1·61035	17·9
17	$C_6H_5(C_6H_4.C_2H_5)Si(C_2H_5)_2$ . .	169–170° C./14 mm.	$D_4^{19·0}$ 0·9840 ; D_4^{20} 0·9831	1·55716	1·56225	1·57559	1·58713	16·8
18	$(C_2H_5)_3Si.C_6H_4.C_2H_5$ . . .	117–118° C./18 mm.	$D_4^{18·2}$ 0·8969 ; D_4^{20} 0·8950	1·50272	1·50671	1·51697	1·52583	20·7

Compounds 1–4 are of the type $C_6H_4Br.Si(OR)_3$, and are obtained by the interaction of p-bromophenyl silicon trichloride and alcohols. Nos. 5–8 are prepared by treating the magnesium compound from p-bromophenyltriethylsilicane with acetaldehyde and higher aldehydes, and are of the type $Si(C_2H_5)_2.C_6H_4.CHR.OH$. Compound 9 occurs in good yield when compound 5 is heated with fuming hydrochloric acid in a sealed tube at 90° C. The magnesium compound of p-bromophenyltriethylsilicane condenses with silicon tetrachloride to form trichloro-p-triethylsilylphenylsilicane (10), which yields bis-p-triethylsilylbenzene (11) when treated with magnesium ethyl bromide. Magnesium p-bromophenyl bromide and phenyl silicon trichloride give phenyl-p-bromophenyl silicon dichloride (13), which is converted by alcohol into (14) and (15).

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TABLE VII.—CRYSTALLOGRAPHIC MEASUREMENTS OF DIPHENYLSILICANEDIOL.

System, *anorthic*. Sub-class, *holohedral*.

$a : b : c = 0{\cdot}5657 : 1 : 1{\cdot}700.$

$\alpha = 90° 2'$; $\beta = 111° 20'$; $\gamma = 87° 27'$.

Forms developed: b (010), m (110), μ ($1\bar{1}0$), c (001), t (013), v ($\bar{1}16$).

TABLE OF ANGLES.

Faces.	No. of Measurements.	Angle Limits.	Mean Value.	Calculated Value.
010 : 110	16	62° 2′–65° 33′	64° 23′	..
110 : $1\bar{1}0$	16	53° 10′–55° 52′	55° 40′	..
$1\bar{1}0$: $0\bar{1}0$	15	59° 34′–61° 37′	60° 51′	60° 57′
010 : 001	22	89° 52′–90° 30′	90° 11′	..
110 : 001	26	70° 28′–71° 16′	70° 55′	70° 56′
$1\bar{1}0$: 001	26	70° 49′–71° 57′	71° 19′	..
010 : 013	3	58° 20′–61° 40′	60° 31′	..
110 : 013	1	59° 25′	59° 25′	60° 1′
$1\bar{1}0$: 013	1	88° 38′	88° 38′	87° 51′

The crystals are prismatic in habit. Of the prism faces b, m and μ, b and μ are well developed, whilst m is but a small face. The angles of the prism zone, namely b m = 64° 23′, m μ = 55° 40′, μ b = 60° 57′, all approximate to 60° and give the crystals a pseudo-hexagonal character. The crystals are terminated by three planes at each end. These are c (001), t (013), and v ($\bar{1}16$). The face c (001) is quite large, whilst t and v are tiny bevels on the edges c b and c μ' respectively. The faces t and v are very bad ones, particularly the latter, from which no trustworthy measurements can be obtained. The faces as a whole are very bad from a goniometrical point of view, as may be seen from the range of the angles in the preceding.

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TABLE VIII.—CRYSTALLOGRAPHIC MEASUREMENTS OF ANHYDROBISDIPHENYLSILICANEDIOL.

System, *anorthic*. Sub-class, *holohedral*.

a : b : c = 0·6536 : 1 : 1·868.

$\alpha = 92° 28'$; $\beta = 115° 40'$; $\gamma = 86° 24'$.

Forms developed : b (010), m (110), μ ($1\bar{1}0$), c (001), q (011), s ($\bar{1}\bar{1}4$).

TABLE OF ANGLES.

Faces.	No. of Measurements.	Angle Limits.	Mean Value.	Calculated Value.
010 : 110	10	61° 5′–62° 1′	61° 36′	..
110 : $1\bar{1}0$	10	60° 10′–61° 33′	60° 58′	..
$1\bar{1}0$: $0\bar{1}0$	10	56° 40′–57° 56′	57° 26′	57° 26′
010 : 011	20	29° 52′–30° 42′	30° 22′	..
110 : 011	24	52° 18′–53° 14′	52° 49′	52° 53′
$1\bar{1}0$: 011	24	105° 44′–106° 39′	106° 8′	106° 14′
010 : 001	18	88° 38′–89° 29′	89° 4′	89° 0′
110 : 001	20	66° 41′–67° 25′	67° 3′	..
$1\bar{1}0$: 001	20	68° 26′–68° 44′	68° 37′	69° 8′
011 : 001	11	58° 8′–59° 9′	58° 38′	..
110 : $\bar{1}\bar{1}2$	24	142° 43′–143° 19′	143° 1′	143° 21′
010 : $\bar{1}\bar{1}2$	24	119° 5′–119° 55′	119° 31′	119° 22′
$1\bar{1}0$: $\bar{1}\bar{1}2$	24	105° 22′–106° 38′	106° 1′	106° 11′

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The forms b, m, and μ constitute a prism zone; the forms b and m are large and μ small. The angles of the prism zone are: b m = 61° 36′, m μ = 60° 58′, μ b′ = 57° 26′. They all approach the value 60°, and so the crystals are pseudo-hexagonal. Of the three terminal forms, c (001) is much the largest, q and s being small faces on the edges b c and m′ c respectively.

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TABLE IX.—CRYSTALLOGRAPHIC MEASUREMENTS OF DIANHYDROTRISDIPHENYLSILICANEDIOL.

System, *anorthic*. Sub-class, *holohedral*.

a : b : c=0·5068 : 1 : 1·491.

Forms developed : b (010), m (110), μ ($1\bar{1}0$), c (001), r (012), μ ($\bar{1}14$).

TABLE OF ANGLES.

Faces.	No. of Measurements.	Angle Limits.	Mean Value.	Calculated Value.
010 : 110	6	66° 42′–67° 21′	66° 58′	..
110 : $1\bar{1}0$	7	51° 4′–52° 4′	51° 39′	..
$1\bar{1}0$: $0\bar{1}0$	10	60° 4′–61° 53′	61° 32′	61° 23′
010 : 001	16	89° 7′–90° 51′	90° 19′	..
110 : 001	8	74° 9′–74° 55′	74° 35′	74° 34′
$1\bar{1}0$: 001	15	74° 16′–75° 28′	75° 1′	..
010 : 012	1	54° 42′	54° 42′	..
110 : 012	1	63° 11′	63° 11′	63° 11′
$1\bar{1}0$: 012	1	94° 50′	94° 50′	93° 54′
010 : $\bar{1}14$	3	67° 34′– 69° 11′	68° 36′	69° 25′
$1\bar{1}0$: $\bar{1}14$	3	120° 28′–124° 2′	122° 47′	120° 57′
110 : $\bar{1}14$	3	103° 44′–105° 14′	104° 27′	103° 0′

The dominant forms are b (010), μ ($1\bar{1}0$), and c (001). Many crystals are simply four-sided prisms terminated by c planes. The prism face m is often missing, and when present it is only small. The face r (012) was present on one crystal only. The form μ ($\bar{1}14$) was only developed on two crystals, and even then the faces were very poor ones. This accounts for divergence between the calculated and measured angles. The crystals may be described as short, stumpy prisms. The prism angles show some approach to hexagonal development: b m=66° 58′, m μ=51° 39′, μ b′=61° 32′.

If in the crystals of diphenylsilicanediol (see Table VII.) t is given the indices (011) instead of (013), then v will become ($\bar{1}12$) instead of (116). The remaining indices would be unchanged. The axial ratios would now be 0·5657 : 1 : 0·5666 instead of 0·5657 : 1 : 1·700.

Similarly if in the crystals of dianhydrotrisdiphenylsilicanediol r is made (011) instead of (012), then μ would be (112) instead of ($\bar{1}14$), and the remaining indices would be unaltered. The axial ratios would be 0·5068 : 1 : 0·7455 instead of 0·5068 : 1 : 1·491.

To bring the axial ratios of the crystals of anhydrobisdiphenylsilicanediol into line, q would have to be made (031) instead of (011), and the ratios would then be 0·6536 : 1 : 0·6227 instead of 0·6536 : 1 : 1·868. The indices of s ($\bar{1}\bar{1}2$) would then become ($\bar{3}\bar{3}2$).

TABLE X.- CRYSTALLOGRAPHIC MEASUREMENTS OF TRIANHYDROTRISDIPHENYLSILICANEDIOL.

System, *orthorhombic*. Sub-class, *bisphenoidal*.

a : b : c = 0·7750 : 1 : 0·4993.

Forms developed : a (100), b (010), m (110), p (111).

TABLE OF ANGLES.

Faces.	No. of Measurements.	Angle Limits.	Mean Value.	Calculated Value.
110 : 010	19	89° 50′–90° 7′	90° 0′	90° 0′
100 : 110	19	37° 21′–38° 12′	37° 48′	37° 48′
010 : 110	19	51° 55′–52° 29′	52° 12′	..
100 : 111	17	59° 54′–60° 17′	60° 7′	60° 3′
010 : 111	18	66° 58′–67° 27′	67° 14′	..
110 : 111	16	50° 34′–51° 13′	50° 48½′	50° 50′
111 : $\bar{1}\bar{1}1$	8	78° 8′–78° 29′	78° 15′	78° 23′
110 : $1\bar{1}\bar{1}$	12	80° 30′–81° 27′	81° 3′	80° 57′

The crystals occur in two well-marked habits. One of these is prismatic, a and b being large faces, whilst the m faces are small. In other cases the crystals are markedly tetrahedral.

TABLE XI.—CRYSTALLOGRAPHIC MEASUREMENTS O TETRA-ANHYDROTETRAKISDIPHENYLSILICANEDIOL.

System, *anorthic*. Sub-class, *holohedral*.

a : b : c=0·5614 : 1 : 0·5770.

α=83° 56′ ; β=103° 52′ ; γ=96° 44′.

Forms observed : a {100}, b {010}, c {001}, m {110}, q {011}, y {1$\bar{2}$0}.

TABLE OF ANGLES.

Faces.	No. of Measurements.	Angle Limits.	Mean Value.	Calculated Value.
010 : 110	4	56° 23′–57° 16′	56° 56′	57° 6½′
110 : 100	3	27° 13′–27° 48′	27° 30′	27° 25′
100 : 1$\bar{2}$0	10	50° 32′–50° 46′	50° 38′	..
1$\bar{2}$0 : 0$\bar{1}$0	6	44° 46′–44° 59′	44° 50½′	..
010 : 001	8	94° 26′–94° 53′	94° 37′	..
110 : 001	6	80° 39′–81° 57′	81° 8′	80° 58′
100 : 001	11	76° 31′–76° 47′	76° 41′	..
1$\bar{2}$0 : 001	12	76° 29′–77° 18′	76° 54½′	76° 57½′
010 : 011	..	..	..	64° 8′
110 : 011	1	65° 27′	65° 27′	..
100 : 011	1	74° 38′	74° 38′	75° 9′
1$\bar{2}$0 : 011	1	98° 31′	98° 31′	99° 3′

The crystals are flat, almost square, plates, the pinacoid a {100} being predominant, and the forms b {010} and c {001} being developed along the edges of the plates.

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TABLE XII.—CRYSTALLOGRAPHIC MEASUREMENTS OF TRIANHYDROTRISDIBENZYLSILICANEDIOL.

System, *oblique*. Sub-class, *holohedral*.

$a : b : c = 2{\cdot}797 : 1 : 1{\cdot}643$; $\beta = 94° 38'$.

Forms developed : a {100}, c {001}, m {110}, s {101}, r {$\bar{1}$01}.

TABLE OF ANGLES.

Faces.	No. of Measurements.	Angle Limits.	Mean Value.	Calculated Value.
100 : 101	9	59° 20′–60° 11′	59° 43′	59° 29′
101 : 001	9	25° 14′–26° 13′	25° 38′	25° 53′
100 : $\bar{1}$00	9	85° 2′–85° 40′	85° 22′	..
001 : $\bar{1}$01	11	27° 2′–28° 4′	27° 38′	27° 47′
$\bar{1}$01 : $\bar{1}$00	9	66° 31′–67° 4′	66° 51′	..
100 : 110	23	70° 0′–70° 36′	70° 14′	70° 16′
101 : 110	33	80° 0′–80° 33′	80° 15′	80° 3′
110 : $\bar{1}$10	16	39° 11′–39° 43′	39° 28′	..
001 : 110	42	88° 13′–88° 54′	88° 30′	88° 27′
$\bar{1}$01 : 110	47	96° 59′–97° 58′	97° 33′	97° 38′

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The crystals are prismatic in habit, being elongated in a direction perpendicular to the diad axis. The m faces in general are much larger than the a faces.

TABLE XIII.—PHYSICAL CONSTANTS OF TIN ALKYLS OF THE TYPE R_3SnR'.

Compound.	Boiling-point. °C.	Density.	Refractive Index.			
			n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.
						° C.
Tin triethyl n-propyl	82/13 mm.	$D_4^{20\cdot6}$ 1·1640	1·46936	1·47273	1·48108	1·48816, at 20·6
Tin triethyl isobutyl	96·5/17 ,,	$D_4^{20\cdot3}$ 1·1390	1·46977	1·47304	1·48132	1·48826, ,, 20·3
Tin triethyl isoamyl	111/18 ,,	$D_4^{18\cdot5}$ 1·1203	1·46917	1·47243	1·48050	1·48739, ,, 18·5
Tin ethyl tri-n-propyl	117·5/23 ,,	$D_4^{21\cdot8}$ 1·1225	1·47053	1·47374	1·48197	1·48890, ,, 21·8
Tin ethyl tri-isobutyl	125/16 ,,	D_4^{21} 1·0779	1·47053	1·47371	1·48167	1·48830, ,, 21
Tin tri-n-propyl isobutyl	128/18 ,,	$D_4^{24\cdot1}$ 1·0841	1·46929	1·47245	1·48042	1·48711, ,, 24·1
Tin tri-isobutyl isoamyl	152·9/16·5 ,,	$D_4^{26\cdot8}$ 1·0356	1·46851	1·47174	1·47984	1·48575, ,, 26·8

TABLE XIV.—PHYSICAL CONSTANTS OF TIN ALKYLS OF THE TYPE $R_2SnR'_2$.

Compound.	Boiling-point. °C.	Density.	Refractive Index.			
			n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.
						°C.
Tin dimethyl di-isobutyl . .	85/16 mm.	$D_4^{20\cdot1}$ 1·1179	1·46037	1·46354	1·47165	1·47851, at 20·1
Tin diethyl di-isobutyl . .	108·2/13 „	$D_4^{30\cdot4}$ 1·1030	1·47036	1·47361	1·48167	1·48846, „ 20·4
Tin diethyl di-isoamyl . . .	131/13·5 „	D_4^{19} 1·0725	1·46957	1·47268	1·48040	1·48694, „ 19

TABLE XV.—PHYSICAL CONSTANTS OF TIN ALKYLS OF THE TYPE $R_2R'SnX$.

Compound.	Boiling-point. °C.	Density.	Refractive Index.			
			n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.
						°C.
Tin diethyl-n-propyl chloride .	108/17 mm.	$D_4^{15\cdot7}$ 1·3848	1·50207	1·50580	1·51524	1·52322, at 15·7
Tin diethyl isoamyl chloride . .	125·5–126·5/13 „	$D_4^{19\cdot9}$ 1·2994	1·49443	1·49805	1·50687	1·51443, „ 19·9
Tin diethyl n-propyl bromide . .	112·2/16 „	$D_4^{21\cdot0}$ 1·5910	1·51759	1·52177	1·53232	1·54129, „ 21·0
Tin diethyl isobutyl bromide . .	122/17 „	$D_4^{20\cdot0}$ 1·5108	1·51194	1·51586	1·50609	1·53464, „ 20·0
Tin diethyl isoamyl bromide . .	137·5/17 „	$D_4^{17\cdot0}$ 1·4881	1·51521	1·51651	1·52653	1·53503, „ 17·0
Tin ethyl di-isobutyl bromide . .	130·6/13 „	$D_4^{19\cdot5}$ 1·4085	1·50452	1·50837	1·51799	1·52609, „ 19·5
Tin ethyl di-isoamyl bromide . .	154–155/16 „	$D_4^{20\cdot0}$ 1·3650	1·50263	1·50631	1·51562	1·52347, „ 20·0

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TABLE XVI.—PHYSICAL CONSTANTS OF SOME TIN ALKYLS.

M.W.	Compound.	M.pt. °C.	B.pt. °C. 13 mm.	Density.	Refractive Index.			
					n_{α}.	n_D.	n_{β}.	n_{H_γ}.
235·2	Tin tetraethyl	−112	78	$D_4^{19·7}$ 1·1988	1·46897	1·47243	1·48099	1·48826, at 19·7° C.
249·2	Tin triethyl n-propyl	..	82	$D_4^{20·6}$ 1·1640	1·46936	1·47273	1·48108	1·48816, „ 20·6° C.
291·2	Tin tetra-n-propyl	..	116	$D_4^{20·2}$ 1·1065	1·47126	1·47448	1·48260	1·48936, „ 20·2° C.
				$D_4^{50·8}$ ..	1·45826	1·46144	1·46939	1·47607, „ 50·8° C.
241·6	Tin triethyl chloride	+ 15·5	94	$D_4^{23·3}$ 1·4288	1·50172	0·60553	1·51510	1·52332, „ 23·3° C.
				D_4^{43} ..	1·49114	..	1·50442	.. „ 43° C.
283·7	Tin tri-n-propyl chloride	− 23·5	123	D_4^{28} 1·2678	1·48754	1·49102	1·49976	1·50707, „ 28° C.
				$D_4^{35·4}$ ..	1·48439	1·48774	1·49648	1·50372, „ 35·4° C.
325·7	Tin tri-isopropyl chloride	+ 15·0	142	$D_4^{24·8}$ 1·1826	1·48235	1·48564	1·49402	1·50098, „ 24·8° C.
367·8	Tin tri-isoamyl chloride	+ 30·2	174	$D_4^{34·2}$ 1·1290	1·47714	1·48040	1·48825	1·49496, „ 34·2° C.
286·0	Tin triethyl bromide	− 13·5	97	D_4^{20} 1·6530	1·52376	1·52812	1·53900	1·54840, „ 20° C.
328·1	Tin tripropyl bromide	− 49	133	$D_4^{25·2}$ 1·4263	1·50263	1·50655	1·51620	1·52437, „ 25·2° C.
370·1	Tin tri-isobutyl bromide	− 26·5	148	D_4^{20} 1·3523	1·50103	1·50460	1·51395	1·52185, „ 20° C.
				$D_4^{41·6}$ ..	1·49175	1·49540	1·50461	1·51246, „ 41·6° C.
412·2	Tin tri-isoamyl bromide	+ 21	177	$D_4^{20·7}$ 1·2613	1·49426	1·49783	1·50649	1·51382, „ 20·7° C.
291·0	Tin trimethyl iodide	+ 3·4	71	D_4^{25} 1·1216	1·56632	1·57238	1·58811	1·60169, „ 28° C.
				D_4^{39} ..	1·55996	1·56586	1·58145	.. „ 39° C.
333·0	Tin triethyl iodide	− 34·5	117	$D_4^{17·5}$ 1·8255	1·55933	1·56486	1·57882	1·59097, „ 17·5° C.
375·1	Tin tri-n-propyl iodide	− 53	141	D_4^{21} ..	1·53609	1·54082	1·55311	1·56358, „ 21° C.
				$D_4^{30·4}$ 1·5960	1·53190	1·53673	1·54884	1·55927, „ 30·4° C.
417·1	Tin tri-isopropyl iodide	..	151	$D_4^{22·2}$ 1·4378	1·51784	1·82221	1·53324	1·54284, „ 22·2° C.
459·2	Tin tri-isoamyl iodide	− 22	182	$D_4^{26·5}$ 1·3777	1·51358	1·51768	1·52820	1·53726, „ 26·5° C.
				$D_4^{30·7}$ ..	1·51184	..	..	1·53540, „ 30·7° C.
336·9	Tin diethyl dibromide	..	..	D_4^{74} 2·0680	1·5507	1·5557	1·5693	1·5808, „ 74° C.
402·8	Tin dimethyl di-iodide	..	..	$D_4^{39·3}$ 2·8582	1·68079	1·69056	1·71680	.. „ 39·3° C.
438·7	Tin tetrabromide	..	..	$D_4^{22·4}$ 3·3602	1·65891	1·66762	1·69087	1·71227, „ 22·4° C.
				$D_4^{37·8}$ ..	1·64979	1·65850	1·68142	1·70247, „ 37·8° C.
251·2	Tin triethyl ethylate	..	82	$D_4^{23·3}$ 1·2394	1·46227	1·46553	1·47382	1·48076, „ 23·3° C.

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TABLE XVII.—PHYSICAL CONSTANTS OF TIN ALKYLS OF THE TYPE $R_3Sn.SnR_3$.

Compound.	Boiling-point.	Density.	Refractive Index.			
			n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.
Hexaethyl-distannane .	161° C./23 mm.	$D_4^{17.8}$ 1·3795	1·53224	1·53738	1·55065	1·56210, at 17·8° C.
Hexa-n-propyl-distannane	143·6° C./15 ,,	$D_4^{19.5}$ 1·2436	1·52112	1·52583	1·53773	1·54806, ,, 19·5° C.
Hexa-isobutyl-distannane	179° C./13·5 ,,	D_4^{59} 1·1330	1·49706	1·50128	1·51191	1·52120, ,, 59° C.
Sym-tetraethyl-dipropyl-distannane . .	165·8° C./15 ,,	$D_4^{16.5}$ 1·3346	1·53042	1·53540	1·54822	1·55945, ,, 16·5° C.
Sym-tetraethyl-di-isobutyl-distannane . .	179° C./15·5 ,,	$D_4^{19.8}$ 1·2919	1·52108	1·52571	1·53772	1·54815, ,, 19·8° C.

TABLE XVIII.—PHYSICAL CONSTANTS OF HETEROCYCLIC TIN COMPOUNDS.

Compound.	Boiling-point.	Density.	Refractive Index.			
			n_{H_α}.	n_D.	n_{H_γ}.	n_{H_λ}.
Tin diethyl - cyclopentamethylene . . .	95° C./14 mm.	$D_4^{19.9}$ 1·2693	1·50298	1·50673	1·51586	1·52357, at 19·9° C.
Tin diethyl - 5 - bromoamyl bromide . . .	190·5° C./16 ,,	D_4^{20} 1·7113	1·54270	1·54707	1·55768	1·55675, ,, 20° C.
Tin triethyl-5-bromoamyl .	155·5° C./15 ,,	D_4^{20} 1·3723	1·50204	1·50563	1·51457	1·52213, ,, 20° C.
Tin triethyl-n-amyl . .	110° C./15 ,,	D_4^{20} 1·1258	..	..	..	..
1 : 10-Bis - triethylstannyl-n-decane	248° C./15 ,,	$D_4^{20.7}$ 1·1887	..	..	..	..
Tin diethyl-n-amyl bromide	135° C./15 ,,	$D_4^{22.3}$ 1·4365	1·50484	1·50866	1·51825	1·52657, ,, 22·3° C.
Tin dimethyl - cyclopentamethylene . . .	64° C./16 ,,	$D_4^{23.1}$ 1·3357	1·49861	1·50242	1·51184	1·51993, ,, 23·1° C.
Tin dimethyl-5-bromoamyl bromide . . .	168° C./15 ,,	D_4^{25} 1·8385	1·54548	1·54983	1·56085	1·57019, ,, 25° C.
Tin trimethyl-5-bromoamyl	124° C./18 ,,	$D_4^{23.4}$ 1·4659	1·49604	1·49976	1·50895	1·51677, ,, 23·4° C.
1 - Trimethylstannyl - 5 - trimethylplumbyl-n-pentane	162° C./18 ,,	$D_4^{23.2}$ 1·6482	1·51822	1·52282	1·53452	1·54473, ,, 23·2° C.
1 · 5-Bis-triethylstannyl - n - pentane . . .	205·5° C./15 ,,	D_4^{20} 1·2654	..	1·5053	$n_F - n_C =$	0·01312, ,, 20° C.

DropBooks

TABLE XIX.—PHYSICAL CONSTANTS OF LEAD ALKYLS OF THE TYPE R_3PbR'.

Compound.	Boiling-point.	Density (vacuum).	$n_F - n_C$.	n_D.
Lead trimethyl ethyl . .	27–28° C./10–11 mm. or 128–130° C./751 mm.	$D_4^{20\cdot2}$ 1·8893	0·01936	1·5132, at 19° C.
Lead trimethyl n-propyl . .	48–49° C./16 mm. or 151–152° C./755 mm.	D_4^{23} 1·7595	0·01805	1·5082, „ 21° C.
Lead trimethyl n-butyl . .	64·5° C./14 mm.	D_4^{24} 1·6740	0·91705	1·5035, „ 22·5° C.
Lead trimethyl isobutyl . .	58–59° C./15 mm. or 165–166° C./769 mm.	$D_4^{23\cdot5}$ 1·6684	0·01675	1·5021, „ 21·2° C.
Lead trimethyl isoamyl . .	70° C./13 mm.	1·5241	0·01553	1·4926, „ 20·3° C.
Lead methyl triethyl . .	70–70·5° C./16 mm.	1·7124	0·01826	1·5158, „ 24·3° C.
Lead triethyl n-propyl , .	97° C./12–13 mm.	1·5948	0·01719	1·5175, „ 19·7° C.
Lead triethyl isobutyl . .	108·2° C./16 mm.	1·5302	0·01686	1·5120, „ 21·5° C,
Lead triethyl isoamyl . .	114·5° C./13 mm.	1·5055	0·01680	1·5118, „ 21·0° C.

TABLE XX.—PHYSICAL CONSTANTS OF LEAD ALKYLS OF THE TYPE R_3PbR'.

Compound.	Boiling-point.	Density.	Refractive Index.				
			n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}	n_F—n_C.
Lead trimethyl isopropyl .	75° C./60 mm.	D_4^{20} 1·7403	1·5042	1·5095	1·5223	1·5335, at 20° C.	..
Lead triethyl sec-butyl .	103° C./13 „	D_4^{15} 1·5360	1·51600	1·52088	1·53310	1·54390, „ 15° C.	0·01703
Lead triethyl isopropyl .	90° C./13 „	D_4^{20} 1·5812	1·5131	1·5181	..	..	0·01773, at 20° C.
Lead triethyl sec-amyl .	121° C./17 „	D_4^{21} 1·4906	1·51065	1·51537	1·52717	1·53712, „ 21° C.	
Lead methyl tri-isoamyl .	..	D_4^{22} 1·3134	1·49226	1·49618	1·50612	1·51477, „ 22° C.	
Lead ethyl tri-isoamyl .	..	$D_4^{19·6}$ 1·2922	1·49425	1·49825	1·50818	1·51669, „ 19·6° C.	
Lead n-propyl tri-isoamyl .	..	D_4^{22} 1·2737	1·49324	1·49703	1·50696	1·51542, „ 22° C.	
Lead isobutyl tri-isoamyl .	..	$D_4^{19·5}$ 1·2522	1·49242	1·49618	1·50597	1·51428, „ 19·5° C.	
Lead methyl tri-isobutyl .	121° C./12 „	$D_4^{19·6}$ 1·3977	1·49883	1·50321	1·51397	1·52324, „ 19·6° C.	
Lead ethyl tri-isobutyl .	..	$D_4^{22·1}$ 1·3758	1·50134	1·50552	1·51636	1·52573, „ 22·1° C.	
Lead n-propyl tri-isobutyl .	..	$D_4^{19·6}$ 1·3505	1·50148	1·50561	1·51631	1·52554, „ 19·6° C.	
Lead tri-isobutyl isoamyl .	..	$D_4^{20·6}$ 1·2976	1·49696	1·50097	1·51118	1·51989, „ 20·6° C.	
Lead methyl tri-n-propyl .	106° C./13 „	$D_4^{22·3}$ 1·5220	1·50456	1·50911	1·52059	1·53058, „ 22·3° C.	
Lead ethyl tri-n-propyl .	118·2° C./14 „	$D_4^{21·3}$ 1·4846	1·50703	1·51149	1·52290	1·53299, „ 21·3° C.	
Lead tri-n-propyl isobutyl .	..	$D_4^{22·6}$ 1·4034	1·50235	1·50673	1·51766	1·52716, „ 22·6° C.	
Lead tri-n-propyl isoamyl .	..	D_4^{21} 1·3810	1·50049	1·50465	1·51535	1·52462, „ 21° C.	

DropBooks

TABLE XXI.—PHYSICAL CONSTANTS OF LEAD ALKYLS OF THE TYPE R_2PbR_2'.

Compound.	Boiling-point.	Density (vacuum).	$n_F - n_C$.	Yield.	n_D.
Lead dimethyl di-n-propyl . .	77–78° C./13 mm.	$D_4^{24.4}$ 1·6230	0·01679	70 per cent.	1·5062, at 23·1° C.
Lead dimethyl di-isobutyl . .	95·5–96° C./13 „	$D_4^{20.6}$ 1·5042	0·01585	70 „	1·5023, „ 20·4° C.
Lead dimethyl di-isoamyl . . .	122–123° C./13 „	D_4^{20} 1·4302	0·01485	75 „	1·5005, „ 20° C.
Lead diethyl di-n-propyl . . .	105° C./13 „	D_4^{25} 1·5285	0·01654	85 „	1·5127, „ 25° C.
Lead diethyl di-sec-propyl. . .	95·5° C./14 „	$D_4^{15.9}$ 1·5358	..	..	..
Lead diethyl di-isobutyl . . .	124° C./13 „	D_4^{22} 1·4455	0·01564	90 „	1·5081, „ 22° C.
Lead diethyl di-isoamyl . . .	142° C./13 „	D_4^{20} 1·3757	0·01473	95 „	1·5041, „ 20° C.

TABLE XXII.—PHYSICAL CONSTANTS OF LEAD ALKYLS OF THE TYPE $R_2PbR'R''$.

No.	Compound.	Boiling-point.	Density (vacuum).	Refractive Index.			
				n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.
1	Lead dimethylethyl-n-propyl	65° C./15 mm.	D_4^{23} 1·6943	..	..	..	..
2	Lead dimethylethyl-sec-propyl	61·2° C./15 ,,	$D_4^{20\cdot6}$ 1·6968	1·50812	1·51327	1·52614	1·53731, at 20·6° C.
3	Lead dimethylethyl-isobutyl	74° C./13 ,,	$D_4^{20\cdot7}$ 1·6234	1·50327	1·50783	1·51982	1·53010, ,, 20·7° C.
4	Lead dimethylethyl-sec-butyl	75° C./14 ,,	D_4^{21} 1·6322	..	..	..	..
5	Lead dimethylethyl-isoamyl	92° C./14 ,,	$D_4^{21\cdot7}$ 1·5579	1·50079	1·50524	1·51602	1·52647, ,, 21·7° C.
6	Lead dimethylethyl-sec-amyl	90° C./15 ,,	D_4^{20} 1·5669	1·50676	1·51139	1·52341	1·53401, ,, 20° C.
7	Lead dimethylpropyl-isoamyl	105° C./15 ,,	D_4^{22} 1·5028	1·49773	1·50201	1·51313	1·52251, ,, 22° C.
8	Lead dimethyl-sec-butyl-isoamyl	111·5–112·5° C./14 mm.	D_4^{22} 1·4709	1·50125	1·50571	1·51686	1·52675, ,, 22° C.
9	Lead diethylmethylpropyl	80·8° C./15 mm.	$D_4^{22\cdot5}$ 1·6399	1·50925	1·51412	1·52638	1·53710, ,, 22·1° C.
10	Lead diethylmethyl-isobutyl	87° C./13 ,,	$D_4^{20\cdot5}$ 1·5805	..	..	..	..
11	Lead diethylmethyl-isoamyl	106° C./15·5 ,,	$D_4^{20\cdot8}$ 1·5225	1·50336	1·50783	1·51921	1·52934, ,, 20·8° C.
12	Lead diethyl-n-propyl-sec-propyl	107° C./17 ,,	$D_4^{22\cdot1}$ 1·5336	1·51047	1·51524	1·52766	1·53842, ,, 22·1° C.
13	Lead diethylpropyl-n-butyl	108° C./13 ,,	$D_4^{20\cdot8}$ 1·5285	..	..	..	..
14	Lead diethylpropyl-isobutyl	110° C./13 ,,	D_4^{20} 1·4890	1·50751	1·51195	1·52353	1·53359, ,, 20° C.
15	Lead diethylpropyl-sec-butyl	115·5° C./14·5 ,,	$D_4^{20\cdot1}$ 1·4962	1·51235	1·51698	1·52896	1·53939, ,, 20·1° C.
16	Lead diethylpropyl-isoamyl	127·5° C./15 ,,	$D_4^{22\cdot1}$ 1·4392	1·50217	1·50655	1·51758	1·52721, ,, 22·1° C.
17	Lead diethylpropyl-sec-amyl	121° C./12 ,,	D_4^{19} 1·4554	1·50948	1·51393	1·52551	1·53571, ,, 19·4° C.
18	Lead diethyl-isobutyl-isoamyl	131° C./14 ,,	$D_4^{21\cdot5}$ 1·3980	..	..	..	..
19	Lead di-isoamylethylpropyl	145·5° C./13 ,,	D_4^{20} 1·3552	..	..	..	..

The following are additional constants to be attached to the compounds as shown :—
No. 1 $.n_D^{21\cdot3}$ 1·5110 ; $n_F - n_C$ 0·01687. No. 4. n_D^{21} 1·5140 ; $n_F - n_C$ 0·01711. No. 10. $d_4^{20\cdot4}$ 1·5812 ; $n_D^{19\cdot5}$ 1·5120 ; $n_F - n_C$ 0·01664. No. 13. $n_D^{20\cdot8}$ 1·5120 ; $n_F - n_C$ 0·01639. No. 18. $n_D^{19\cdot3}$ 1·5053. No. 19. $n_D^{18\cdot8}$ 1·5039 ; $n_F - n_C$ 0·01524.

PropBooks

TABLE XXIII.—PHYSICAL CONSTANTS OF MIXED LEAD ALKYLS OF THE TYPE $Alk_3Pb.Ar$.

Compound.	Boiling-point.	Density (vacuum).	Refractive Index.				
			n_{H_α}.	n_D.	n_{H_β}.	n_{H_γ}.	
Lead trimethyl phenyl	104° C./13 mm.	$d_4^{28\cdot7}$ 1·7342 ; d_4^{20} 1·7376	1·5753	1·5816	1·5988	1·6138, at 23·7° C.	..
Lead trimethyl o-tolyl	117·5–118° C./13 mm.	$d_4^{21\cdot4}$ 1·7395 ; d_4^{20} 1·7408	1·5734	1·5793	1·5964	1·6095, „ 21·4° C.	..
Lead trimethyl p-tolyl	118–119° C./13 „	d_4^{20} 1·6826 ; $d_4^{21\cdot5}$ 1·6812	1·5672	1·5732	1·5895	1·6039, „ 20° C.	..
Lead triethyl phenyl .	135° C./12 mm.	$d_4^{21\cdot1}$ 1·5920 ; d_4^{20} 1·5931	1·5698	1·5757	1·5917	1·6057, „ 20° C.	..
Lead triethyl o-tolyl .	153·5° C./13 „	$d_4^{22\cdot2}$ 1·5832 ; d_4^{20} 1·5853 ; $d_4^{21\cdot5}$ 1·5839	1·5682	1·5740	1·5897	1·6035, „ 21·5° C.	..
Lead triethyl p-tolyl .	154° C./13 „	$d_4^{24\cdot8}$ 1·5237 ; d_4^{20} 1·5281 ; d_4^{22} 1·5262	1·5629	1·5686	1·5842	1·5979, „ 22·0° C.	n_D^{20} 1·5695
Lead triethyl benzyl .	149–150·5° C./13 mm.	d_4^{23} 1·5396 ; 1·5374	..	..	..	..	$n_D^{21\cdot4}$ 1·5851 1·5843
Lead triethyl α-naphthyl . .	176° C./13 mm.	..	..	..	..	..	..

Lead triethyl α-naphthyl splits off naphthalene at its boiling-point.
Lead trimethyl benzyl boils at 124° C. with much decomposition.

TABLE XXIV.—PHYSICAL CONSTANTS OF HETEROCYCLIC LEAD COMPOUNDS.

Compound.	Boiling-point.	Density (vacuum).	n_{D}.	$n_F - n_C$.
Lead diethylcyclopentamethylene	111° C./13·5 mm.	D_4^{20} 1·6866	n_D^{20} 1·5484	0·01770
Lead triethyl-5-bromoamyl	166° C./13 ,,	D_4^{20} 1·6851	n_D^{20} 1·5374	0·01663
Lead triethyl-n-amyl	121° C./15 ,,	D_4^{20} 1·4823	n_D^{20} 1·5097	0·01608
1 : 5-Bis-trimethylplumbyl-n-pentane	166·5° C./14 ,,	$D_4^{23·5}$ 1·9448	$n_D^{23·5}$ 1·5571	0·01940

DropBooks

*

NAME INDEX.

Abelmann, 68, 196, 197.
Acree, 5,
Adams, 40, 42, 94, 190, 215.
Alexeyeff, 19, 21.
Allpress, 77.
Anderson, 217.
Aronheim, 73, 77, 87, 322–324.
Ashley, 317, 324, 340, 345, 346.
Auld, 53, 56, 144, 146.

Balbiano, 143, 154, 155, 200.
Bamberger, 32, 75, 90, 158.
Banús, 79.
Bauermeister, 82, 97, 99, 222.
Bauerschmidt, 210.
Becker, 88, 93, 225, 228.
Becker, R., 317, 322, 326, 327, 329.
Beckmann, 11.
Béhal, 188.
Beilstein, 19, 21.
Bernardi, 125, 132.
Berthelm, 221, 235, 237.
Berthelot, 31, 34.
Bessl, 165.
Bewad, 18, 19, 22, 26.
Bielenberg, 74, 84.
Biginelli, 181.
Biilmann, 50, 54, 59, 64, 66, 67, 176, 181.
Biltz, 181, 186, 187, 189.
Bjerrum, 176.
Blaise, 26, 142.
Blaisi, 88, 91.
Bleekrode, 232.
Blumenthal, 173, 176.
Bocchi, 129, 133.
Boedecker, 168.
Bogert, 217.
Bogomolez, 24.
Bohm, 24.
Bönitsch, 112, 139.
Braicovie, 233.
Brame, 181.
v. Braun, 208.
Bredig, 305.
Breest, 181.
Brieger, 132, 133, 156, 158, 166, 178.
Buchner, 65.
Buckton, 13, 18, 21, 30–36, 39–42, 232, 301, 313, 333, 336.
Bullard, 314, 319, 320, 321, 328.
Burkard, 181.
Buroni, 166.
Burton, 106, 114.
Butlerow, 16–18, 23, 25, 333.
Bygdén, 247, 250–252, 259, 262–264, 282, 362.

Cahours, 11–13, 15, 18, 20, 23, 24, 33, 36, 37, 43, 220, 232, 233, 302, 304–310, 314, 333, 336.
Calingäert, 339.
Callis, 304, 305.
Calmels, 20, 32.
Calvert, 11.
Calvery, 38, 39, 43, 44, 77.
Campisi, 79.
Cantapulo, 16, 19, 25.
Carani, 118.
Carius, 21.
Cauer, 263, 269.
Caven, 247.
Cecchetti, 133.
Chalkley, 104, 147, 156, 206.
Challenger, 77, 264, 266.
Chambers, 13, 316, 322, 324, 329.
Chapman, 19, 21, 33, 37.
Chattaway, 82.
Cinsa, 213.
Cocconi, 140.
Coffey, 92, 93, 107, 108.
Coffmann, 5.
Collie, 26, 301, 302.
Corey, 291.
Cowper, 47.
Crafts, 13, 18, 20, 250, 252.
Crymble, 31, 34, 40.
Csabay, 340, 346, 347.
Curtius, 65.

Davies, 265.
Dean, 68.
Delacre, 22, 26.
Demarçay, 306, 307, 310.
Demuth, 20.
Denigès, 47, 54, 181.
Dennis, 291–295, 297, 298.
Desesquelle, 140.
Diels, 191.
Dilthey, 267, 270, 271, 275.
Dimroth, 33, 41, 72, 90–93, 97, 101, 104, 105, 112, 121, 139–144, 149, 151, 155, 162, 166, 196, 197, 204, 208.
Disselkamp, 337, 345.
Ditmar, 31, 32, 40, 41.

Dreher, 73–76, 78, 87–90.
Dreschel, 13.
Drew, 294–297.
Druce, 311–313.
Dufford, 11.
Dünhaupt, 34, 41, 42.
Duppa, 17, 19, 20, 22, 25, 31–33, 35, 36, 38, 44.
Durand, 12, 15.

Ehrhartinger, 213.
Edouardoff, 267, 270, 271, 275.
Ehrenfeld, 108.
Ehrhard, 73.
Eichor, 39, 44.
Erdmann, 187.
Essers, 58, 181.
Evans, 317, 324, 340, 345, 346.

Fahlberg, 234.
Fiegel, 49.
Filetti, 16, 19, 25.
Finkelstein, 13.
Finzi, 97, 126.
Fischer, 33, 40, 65, 73.
Fleck, 12, 15, 16, 33, 36, 74.
Fleming-Struthers, 54, 196, 198.
Forster, 73.
Foster, 294–297.
Fourneau, 146, 147.
Franchimont, 76, 87.
Frankland, 11, 12, 13, 16–23, 25, 27, 31–33, 35, 36, 38–41, 44, 219, 223–225, 301–303, 309, 313, 333.
Franklin, 40.
Freund, 17, 23.
Friedel, 13, 18, 20, 250, 252, 256, 257, 259, 263, 283, 284.
Fromm, 27.
Fujimoto, 68.
Fürstenhoff, 13, 232.

Gabarini, 126.
Gajewski, 198.
Gal, 20, 23.
Gannagé, 81, 95, 96.
Gauerke, 42–44.
Gazarolli-Thurnlakh, 18, 22, 24, 26.
Genssler, 55, 57, 103, 184.
Genzken, 93.
Gerhardt, 47.
Gersch, 167, 168.
Ghira, 31, 34, 301, 333.
Gibson, 4, 9, 79, 94.
Gilman, 11, 12, 14–16, 340.
Gladstone, 18, 19, 23, 24, 301.
Glinsky, 190.
Godchaux, 122.
Goddard, A. E., 36–38, 43, 76, 85, 98, 220–222, 235–240, 242–244, 302, 317, 322, 324, 338, 340, 342, 343, 345, 346, 350.
Goddard, D. (Mrs), 76, 221, 222, 302, 317, 322, 338, 340, 342, 343, 345.
Goldacker, 126.
Goret, 36, 43.
Goriainow, 21.
Gould, 31, 34, 36, 37, 40, 43, 44.
Grabowski, 21.
Graeff, 77, 87.
Grafflin, 78, 79, 88.
Graham, 20.
Granichstädten, 22, 23.
Greenlaw, 17.
Greer, 304, 313, 315.
Grignard, 196, 197, 233.
Grigorowitsch, 23, 54.
Grillo, 213.
Grimm, 302, 310.
Grosse, 3, 5, 8, 221, 235, 242, 243.
Grüttner, 5, 12, 13, 14, 16, 26, 28, 33, 76, 77, 81, 85, 86, 88, 92, 94–96, 208, 234, 253, 269, 291, 302, 303, 305, 307, 311, 314, 317, 325, 326, 333–338, 341–343, 348, 351.
Grutzner, 140.
Guichard, 35.
Guntz, 19.
Gwosdow, 26.

Haas, 189, 190.
Hackford, 270, 271, 282, 283.
Hager, 4, 5, 39.
Hallwachs, 12, 232.
Hamilton, 78, 93.
Hammond, 106.
Hance, 291, 292.
Hauke, 104.
Hansen, 221, 237.
Hanson, 205.
Hantzsch, 53, 56, 144, 146, 198.
Harden, 208.
Hart, 158, 254.
Hartwig, 13, 221, 237.
Hasenbäumer, 77.
Hasse, 17, 19.
Heidelberger, 113, 129, 205.
Hein, 13, 34, 73, 78, 80, 81, 122.
Heller, 304, 312.
Hellon, 64.
Henry, 22–24, 45.
Henry, T. A., 152, 153, 192–195.
Herman, 26.
Herrera, 217.
Herrmann, 141.
Heumann, 76, 87.
Heuter, 164, 168, 171.
Hill, 42–44.
Hilpert, 5, 12–14, 16, 26, 28, 31–33, 40, 41, 76, 77, 85, 86, 88, 92, 94, 96, 208, 234.
Hinsberg, 21.
Hirschfelder, 158.
Hjortdahl, 305, 306, 308–310.
Hobson, 17, 20.
Hochwalt, 339.
Hodgson, 144.
Hofman, 13, 20.
Hofmann, 45, 48–50, 52–54, 60, 62, 64, 180–182, 184–188, 190.

DropBooks

Holtz, 4, 5, 6.
Holzmann, 32.
Howard, 31.

Ipatiew, 16.

Jacobs, 113, 129, 205.
Jacobsohn, 118, 121, 123, 124.
Jacobson, 80, 81.
Japp, 23.
Jenkins, 233.
Jensen, 74, 84.
Job, 25.
Johnson, 188, 189.
Jolibois, 333.
Jones, 32, 34, 38, 79, 80, 95.
Jürgens, 105.

Kahlfuss, 19.
Kalle, 23.
Kaulfuss, 16.
Kawamura, 3, 6, 8.
Keiser, 181.
Kekulé, 76, 87.
Kelbe, 82.
Kenner, 106.
Kharasch, 63, 64, 75, 78, 79, 80, 86, 88, 104, 105, 118, 121, 123–125, 147, 156, 159, 206.
Khotinsky, 93, 95, 219, 223, 225, 226, 229, 284.
Kipping, 248, 250, 254, 258, 262–272, 275, 278–285, 287–290, 307, 318, 320, 323, 325.
Kirmreuther, 188, 190.
Klein, 131.
Klippel, 336, 338.
Klug, 183.
Köchlin, 76, 87.
Köten, 42, 94, 190.
Köthner, 187.
Krafft, 77.
Krassowski, 13, 33.
Kraus, 3, 6, 8, 31, 266, 294–297, 304, 305, 313–315, 321, 328.
Krause, 9, 12, 13, 27, 31, 34, 219–221, 224–229, 231, 233, 235, 242, 243, 263, 291, 302–305, 307, 308, 311, 317, 318, 321–323, 325–327, 329, 333–338, 341–345, 348, 350, 351.
Kulmiz, 306.
Kunz, 79, 93, 94.
Kursanov, 96.
Kutscheroff, 54, 187.

Lachmann, 16, 18, 22, 23, 25, 292.
La Coste, 35, 77.
Ladenburg, 13, 17, 23, 73, 77, 79, 87, 250, 251, 253–259, 263, 266, 268, 269, 279, 283, 284, 301, 304–306, 309, 314, 321, 326.
Landolt, 32.
Lang, 22.
Lasserre, 53, 54, 57.
Laubengayer, 291.
Lavroff, 11.
Law, 320, 327.
Lawrance, 13, 21, 301, 333.
Le Comte, 181.
Lederer, 342.
Lehmardt, 308, 311, 312.
Leone, 233.
Letts, 26, 301, 302.
Leuck, 205.
Ley, 40, 64, 67.
Leys, 53, 155.
Liese, 173.
Link, 77.
Linnemann, 33, 44.
Lippmann, 34, 42.
Lloyd, 250, 266, 272, 279, 284.
Löhr, 12, 13, 15, 16, 27, 32, 33, 36.
Löloff, 142.
Lommen, 118.
Louise, 37, 232, 233.
Löwig, 309, 313, 336.
Luff, 267, 271, 280, 281.
Lwow, 17, 21.
Lyons, 77.

M'Cleland, 74, 80.
M'Ewen, 188, 189.
Maguire, 181.
Mälirlein, 190.
Mameli, 140, 149, 151, 152, 154.
Mameli-Mannessier, 151.
Mamlock, 22.
Manchot, 58, 142, 150, 154, 155, 183, 184, 186, 189, 190.
Marcus, 3, 6, 8.
Mark, 7.
Marker, 86.
Markownikoff, 24.
Marquardt, 13, 24, 25, 37, 38.
Marsden, 262–264, 269, 280.
Marsh, 54, 196, 198.
Martin, 254, 258, 266, 269, 272, 284.
Marvel, 4, 5, 31, 34, 36, 37, 39, 40, 43, 44 178.
Maschmann, 149, 176.
Matsumiya, 96.
Matthews, 31.
Maynard, 31, 39, 41, 72, 90, 91.
Meads, 268, 283.
Melamed, 93, 95, 219, 223, 225, 229, 231.
Melser, 252, 254, 256, 259, 269, 283, 284.
Merck, 151.
Meves, 62.
Meyer, V., 20, 221, 235, 237, 311.
Meyer, 235, 333.
Michael, 25, 26, 64.
Michaelis, 35, 73, 76–82, 87, 92, 93, 95, 121, 122, 141, 143, 225, 227, 228, 229,
Michetti, 117.
Middleton, 139–141, 143, 192, 196.
Midgley, 339.
Miller, 23.
Mills, 215.
Mitchell, 203, 204.
Moller, 335, 338, 343.
Moore, 22,
Morgan, 294–297.

Morgunow, 13, 303.
Morics, 81, 96.
Muller, 32.
Munnn, 186, 187.
Murray, 267.

Nef, 189.
Nieuwland, 181.
Nightingale, 11
Nitsche, 219. 224 226.
Normand, 333.
Nyberg, 63.

Ochs, 6.
Odling, 13, 33, 232.
Oliveri-Mandalà, 192, 210.
Oppenheim, 13, 33, 64. 173.
Oppenheimer, 54.
Ornsdorff, 292 295. 297. 298.
Otto, 32, 34. 41, 42. 73, 74 76, 79, 81, 87 91. 93. 96. 97.

Paderi, 210.
Paolini, 143, 151, 154. 155, 158, 200.
Pape, 13, 23, 24, 250, 251, 253, 255, 257.
Paternò, 21, 22.
Pawlow, 17. 18. 22. 23.
Peachey, 13, 301, 303, 307, 308, 311, 312.
Pebal. 19.
Peratoner, 21.
Perkin. 181.
Pesci, 73–75, 91, 112, 113. 116, 120–124, 126, 131, 132, 162 164.
Peters, 77, 78, 87, 88, 93, 198.
Petterson, 62.
Pfeiffer, 73, 301, 308 313, 316, 323, 333, 335 338, 340, 343, 345.
Piccard, 125, 206.
Piccinini, 112, 124.
Pickens, 11.
Pigorini, 124.
Plimpton, 181.
Pohland, 317, 323, 325, 327, 336, 344.
Poleck, 186.
Polis, 259, 262, 266, 267, 269, 316, 339, 340, 345-347.
Ponzio, 25, 37.
Pope, 4, 9, 13, 79, 94, 301, 303, 307, 308, 311, 312.
Popper, 25.
Prager, 63.
Proskouriakoff, 144 146, 156, 168, 204.
Prussia, 125.
Purvis, 74, 80.

Quincke, 232.

Rabinerson, 121, 141.
Racky, 284.
Raffo, 125.
Ragosin, 24.
Raiziss, 144–146, 156, 168, 204.
Rathke, 19.
Reese, 73, 88.
Reich, 9, 25.
Reinkober, 189.
Reissaus, 344, 348, 350.
Reissert, 106.
Reitzenstein, 112–114, 131, 139.
Renning, 284.
Renshaw, 17.
Renwanz, 318, 341.
Retter. 31, 34. 73, 78, 80, 81, 122.
Reynolds, 54, 57.
Reynoso, 47.
Richter, 227, 228.
Rieth, 19, 21.
Robinson, 319–321, 340.
Robison, 258, 268, 270, 275
Roeder, 88, 91, 142.
Roman, 215.
Rosen, 266.
Rosenthaler, 68.
Rossi, 125, 129, 133.
Rother, 129.
Roux, 37, 232, 233.
Rugheimer, 314.
Rupp, 141, 151, 167.
Ruspaggiari, 112, 124.

Sachs, 88, 89, 162–165, 213
Saizew, 21.
Sakauri, 40, 45, 46.
Sand. 50, 52, 55, 57, 59, 60, 103, 180, 181, 183–185, 201–203, 287.
Sandborn, 177.
Saytzeff, 190.
Schafarik, 12, 13, 232.
Scherer, 13. 316, 322, 324, 326, 328.
Schlenk, 3–8, 33, 122, 284.
Schlöttig, 342, 351.
Schmitt, 20.
Schmitz, 317, 318, 341, 343, 345, 348, 350, 351.
Schnurmann, 301, 302, 316, 323.
Schoeller, 58, 59, 65, 66, 126, 129, 164, 171, 173, 177, 184.
Scholl, 63.
Schon, 19.
Schorigin, 5, 33, 35, 38.
Schorlemmer, 34, 42.
Schrauth, 58, 59, 65, 66, 126, 129, 164, 171, 173, 177, 184, 210.
Schröeder, 39, 41.
Schtscherbakoff, 24, 36, 37.
Schulemann, 132, 133, 158, 178.
Schulte, 35.
Schultze, 82.
Schulze, 11, 12, 14-16.
Schwalbe, 101.
Schwarze, 77, 87.
Seidel, 32, 35, 39, 41.
Seiler, 190.
Sell, 34, 42.
Selmi, 47.
Seregenkoff, 284.
Sessions, 304, 314.
Sharp, 152, 153, 192–195.
Singer, 59, 60, 181, 183, 201–203.
Smith, 37.
Smith, C., 203, 204.
Smith, H., 307, 318, 320, 323, 325.

DropBooks

Sneed, 39, 41.
Sobero, 47.
Söderbäck, 74, 89.
Sperry, 215.
Ssimonowitsch, 16, 19.
Ssokoloff, 25, 37.
Stamm, 113, 131.
Staveley, 63, 64.
Steinkopf, 42, 63, 74, 75, 82–84, 86–89, 94, 96–101, 222.
Stock, 223, 224.
Stoehr, 50, 52, 183.
Strecker, 40, 42, 309.
Struensee, 177.
Sulda, 35, 42, 76.

Tabern, 292–295, 297, 298.
Tafel, 37, 38, 43, 335.
Tartarini, 132.
Taurke, 250, 251, 253, 256.
von Than, 45.
Thiele, 190.
Thomas, 234.
Thümmel, 186.
Thurman, 78, 79, 93.
Tiffeneau, 81, 95, 96.
Tolkatschew, 18.
Travers, 181.
Tribe, 18, 24.
Truskier, 73, 333, 336, 337, 340, 345.

Uthemann, 191.

Vecchiotti, 112, 116–118, 130, 131.
Vila, 146, 147.
Volhard, 97, 99.
Vyle, 268.

Waga, 16.
Wagler, 34, 73, 78, 80, 81, 122.
Wagner, 21, 22, 24.
Walden, 34.
Wanklyn, 5, 16, 20, 21, 27, 45.
Wayler, 31.
Weelmizen, 192.
Weller, 80, 95.
Wendt, 9, 12, 220, 233.
Werner, 22. 23, 32, 34, 40, 79, 80, 95, 309.
White, 207.
Whitmore, 78, 79, 93, 108, 122, 134, 139–141, 143, 162, 164, 192, 205.
Wibaut, 105.
Wichelhaus, 13, 19.
Widdowson, 254.
Wilcox, 23.
Willgerodt, 35, 41, 76, 87, 88.
Winkler, 13, 292, 293.
Wischin, 20.
Witt, 59.
Wolff, 79, 95.
Wolffenstein, 22.
Woodward, 162, 164.
Worobjeff, 16.
Wrenshall, 68.
Wunstorf, 168.
Wurtz, 21, 74, 79.

Zechmeister, 340, 346, 347.
Zeidler, 223, 224.
Zeiser, 36, 79.
Zelinsky, 26.
Zinin, 44.

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SUBJECT INDEX.

N.B.—Index is arranged under headings of elements placed in their order of appearing in the Periodic Classification. Where more than one reference is given those references in italics indicate where the preparation and properties of the compound in question may be found.

Lithium.

Lithium *iso*amyl, 5.
,, *n*-butyl, 4.
,, ethyl, 3, *4*.
,, methyl, 3, *4*.
,, phenyl, 3, *5*.
,, triphenylmethyl, 5.

Sodium.

Sodium *iso*amyl, 38.
,, *p*-anisyl-biphenylene-methyl, 8.
,, benzyl, 6.
,, biphenylene-phenyl-methyl, 7.
,, di-biphenylyl-α-naphthyl-methyl, 7.
,, ethyl, *5*, 35.
,, methyl, *5*, 33.
,, phenyl, 6.
,, phenyl-biphenylyl-α-naphthyl-methyl, 7.
,, triphenylmethyl, 3, *6*.

Potassium.

Potassium triphenylmethyl, 8.

Rubidium.

Rubidium ethyl, 8.
,, triphenylmethyl, 8.

Cæsium.

Cæsium ethyl, 8.
,, triphenylmethyl, 9.

Copper.

Cuprous phenyl, 3, *9*.

Silver.

Silver phenyl, 4, *9*.
,, ,, , compound with silver nitrate, *319*, *351*.

Gold.

Amminodiethylauric bromide, 10.
Diethylauric bromide, 3, *9*.
Ethylauric dibromide, 10.

Calcium.

Calcium, organic complexes of, 11.

Beryllium.

Beryllium *n*-butyl iodide, 15.
,, di-*n*-butyl, 15.
,, diethyl, 11, *14*, 36.

DropBooks

Beryllium dimethyl, 12, *14*.
,, diphenyl, 15.
,, dipropyl, 11, *15*, 37.
,, di-*p*-tolyl, 15.
,, ethyl bromide, 15.
,, ,, chloride, 15.
,, ,, iodide, 15.
,, methyl iodide, 12, 14, *15*.
,, phenyl iodide, 12, *15*.

Magnesium.

Magnesium diethyl, 12, *16*, 36.
,, dimethyl, *15*, 33.
,, diphenyl, 12, *16*, 76.
,, dipropyl, 16.

Zinc.

Zinc di-*iso*amyl, 12, *25*, 38.
,, ,, , physical constants of, 357.
,, di-*iso*butyl, 24.
,, ,, , physical constants of, 357.
Zinc diethyl, 8, *18*, *19*, 20, 25, 26, 29, 33, 36, 221, 224, 237, 250, 251, 255–257, 259, 263, 292, 301, 302, 332, 333.
,, ,, , reactions of, 20–23.
,, ,, , physical constants of, 357.
,, dimethyl, 12, *16*, *17*, 21, 25, 27, 31, 33, 223, 248, 258, 303, 333.
,, ,, , reactions of, 17, 18.
,, diphenyl, 13, *26*, 76, 316.
,, dipropyl, *23*, 37, 250, 302.
,, ,, , physical constants of, 357.
,, di-*iso*propyl, 24.
,, ethylate, 18.
,, ethyl *iso*butyl, 357.
,, ethyl iodide, 25.
,, ,, *n*-propyl, 357.
,, ethyl trichloroethylate, 26.
,, methylate, 17.
,, methyl ethylate, 18, *25*.
,, ,, iodide, 16.
,, ,, methylate, 17, *25*.
,, *iso*propyl *iso*amyl, 357.
,, *n*-propyl *iso*butyl, 357.
,, *iso*propyl iodide, 26.

Cadmium.

Cadmium di-*iso*amyl, *28*, *358*, *359*.
,, di-*n*-butyl, *28*, *358*, *359*.
,, di-*iso*butyl, *28*, *358*, *359*.
,, diethyl, *27*, 36, *358*, *359*.
,, dimethyl, *27*, *358*, *359*.
,, diphenyl, 14, *28*, 76.
,, di-*n*-propyl, *28*, *358*, *359*.

Mercury.

Acetaldehyde, mercuration of, 47.
m-Acetaminobenzoic acid, mercuration of, 172.
p-Acetaminophenylmercuric acetate, chloride, hydroxide, sulphate, *124*, *125*.
Acetanilide, mercuration of, 124.
Acetic acid, ,, ,, , 58.
,, acids, substituted, merouration of, 64.
Acetone, reaction with mercuric cyanide, 54.
,, ,, ,, ,, acetate, 55.
Acetophenone, mercuration of, 196.
Aceto-diethyl-methyl-mercuric chloride, 65.

Aceto-dimethyl-methyl-mercuric chloride, 65.
Acetoxymercuri-aceto-*o*-toluidide, 130.
,, ,, ,, -*m*- ,, , 131.
6- ,, ,, ,, ,, ,, , 131.
,, ,, -acetylanthranilic methyl ester, chloride, *170*, *171*.
,, ,, -*p*-anilinobenzoic ethyl ester, chloride, sulphide, 164, 174, *175*.
,, ,, ,, ,, ,, ,, ,, , mercuric acetate salt of, 174.
2- ,, ,, *p*-*iso*amylphenol, 153.
p- ,, ,, aniline, compounds from diazotised, 205.
o- ,, ,, anisole, *141*, 142.
p- ,, ,, ,, , 141, *142*.
,, ,, -anthranilic methyl ester, 169.
,, ,, -benzeneazo-*p*-cresol, chloride, 204.
8(?)- ,, ,, -β-benzeneazo-α-naphthol, 204.
4-*p*- ,, ,, benzeneazo-1-naphthylamine-5-sulphonic acid, 205.
,, ,, ,, -*o*-nitrophenol, bromide, 204.
p- ,, ,, ,, -phenol, 205.
p- ,, ,, ,, -resorcinol, 205.
3(?)- ,, ,, -benzidine, hydrochloride, 132.
,, ,, -*bis*-benzeneazo-α-naphthol, 204.
,, ,, -*p*-bromodimethylaniline, 111, *122*.
α- ,, ,, -β-*iso*butoxy-β-phenylpropionic methyl ester, anhydride, 178.
2- ,, ,, -*p*-*tert*.-butylphenol, 153.
,, ,, carvacrol, 152.
2- ,, ,, -*p*-chloroacetanilide, 120.
o- ,, ,, -*p*-chloroaniline, acetyl derivative, hydroxide, chloride, 118.
p- ,, ,, -*o*- ,, ,, , hydroxide, acetyl derivative, 117.
o- ,, ,, -*p*-cresol, 137, *150*.
4- ,, ,, -*o*-cresol, chloride, nitrate, 149.
6- ,, ,, ,, ,, ,, ,, , 149.
4- ,, ,, -3-diacetoxymercuriphenyl-5-pyrazolone, dichloride, 213.
p- ,, ,, -diacetyl-*o*-nitraniline and acetyl derivative, 119.
6- ,, ,, -2 : 4-dichloroaniline, acetyl derivative, chloride, hydroxide, 111, *118*.
4- ,, ,, 4′-diethylaminoazobenzene, 205.
4- ,, ,, -*m*-dimethylaminoanisole hydrochloride, 147.
4- ,, ,, 4′-dimethylaminoazobenzene, 205.
4- ,, ,, -*m*-dimethylaminophenol, 147.
4- ,, ,, -*m*-dimethylaminophenyl acetate, 137, *147*.
,, ,, -dimethylanthranilic methyl ester, chloride, bromide, iodide, 172.
,, ,, -dimethyl ether, chloride, 184.
,, ,, dimethyl-*p*-toluidine, chloride, bromide, iodide, hydroxide, nitrate, 132.
p- ,, ,, -diphenylamine, chloride, hydroxide, 125.
α- ,, ,, -β-ethoxy-β-phenylpropionic methyl ester, chloride, bromide, iodide, internal anhydride, 177.
α- ,, ,, -β-ethoxy-β-phenylpropiophenone, 196.
,, ,, -ethylanthranilic ethyl ester, methyl ester, 172,
,, ,, -ethylmethyl ether, 58, *184*.
,, ,, formic ethyl ester and derivatives, 58.
,, ,, ,, methyl ,, ,, ,, , 58,
2- ,, ,, -3-hydroxybenzaldehyde, 193.
α- ,, ,, -β-hydroxysuccinic acid, derivative of, 67.
2- ,, ,, -4-hydroxy-2-methyl-5-*iso*propyl-benzaldehyde, 152.
2- ,, ,, -3-hydroxy-tetrahydronaphthalene, 103.
4- ,, ,, -*o*-iodoaniline, hydroxide, iodide, 118.
2- ,, ,, -*p*- ,, ,, ,, , acetyl derivative, 118.
2- ,, ,, -6-iodothymol, chloride, bromide, oxide, 152.
α- ,, ,, -β-methoxy-β-phenyl-*p*-chloropropiophenone, 197.
α- ,, ,, ,, ,, -β-phenylpropionic ethyl ester, benzyl ester, 178.
α- ,, ,, ,, ,, ,, ,, ,, *l*-menthyl ester, chloride, bromide, 178.
α- ,, ,, ,, ,, ,, ,, ,, methyl ester, chloride, bromide, iodide, 177.
α- ,, ,, ,, ,, -β-phenylpropiophenone, 196.
,, ,, methylanthranilic methyl ester, chloride, bromide, iodide, 171.

DTM Books

1-Acetoxymercurimethyl-4-bromo-1 : 2-dihydrobenzofurane, 216.
1- „ „ „ -1 : 2-dihydrobenzofurane, chloride, bromide, iodide, 215.
p-Acetoxymercuri-methyldiphenylamine, hydroxide, 126.
3- „ „ -1-methylindole, 214.
1-Acetoxymercurimethyl-6-methyl-1 : 2-dihydrobenzofurane, 216.
1- „ „ „ -5- „ „ -, „ , 216.
1- „ „ „ -4- „ „ „ „ , 216.
3-Acetoxymercuri-2-methyl-1-phthalyl indole, 214.
„ „ -*N*-methylthiodiphenylamine, 126.
1- „ „ -β-naphthol, 138, *158*.
2- „ „ -1-naphthol-4-sulphonic acid (sodium salt), 138, *157*.
1- „ „ -2- -6- „ „ „ „ , 138, *158*.
1- „ „ -β-naphthylamine, 133.
p- „ „ -*o*-nitroaniline, 111, *118*.
p- „ „ -*m*- „ „ , 119.
o- „ „ -*p*- „ „ , acetyl derivative, *119*, *120*.
8(?)- „ „ -2-nitro-4-benzeneazo-α-naphthol, 204.
8(?)- „ „ -4- „ -2- „ „ „ , 204.
5- „ „ -3-nitro-4-hydroxybenzaldehyde, 194.
„ „ -2- „ -3- „ „ , 195.
o- „ „ phenetole, chloride, bromide, iodide, 143.
p- „ „ „ , *143*, 144.
o- „ „ phenol, hydroxide, internal oxide, bromide, iodide, nitrate, sulphate, 140.
p- „ „ phenol, hydroxide, bromide, iodide, nitrate, sulphate, 140.
2-Acetoxymercuriphenylglycine, ethyl ester, 127.
α-Acetoxymercuri-β-propoxy-β-phenylpropionic methyl ester, chloride, bromide, iodide, internal anhydride, 177.
α- „ „ -β-*iso*propoxy-β-phenylpropionic methyl ester, anhydride, *177*, *178*.
„ „ -salicylic methyl ester, 162, *167*.
„ „ „ ethyl „ , 167.
2- „ „ thymol, chloride, bromide, nitrate, oxide, sulphate, *151*, *152*.
6- „ „ „ , bromide, hydroxide, „ „ „ , 152.
5- „ „ toluene-2-azophenol, 205.
„ „ *o*-tolylglycine ethyl ester, 128.
„ „ *m*- „ „ „ „ , anhydride, 129.
„ „ *p*- „ „ „ „ „ , 129.
5- „ „ -*o*-toluidine, 129.
6- „ „ -*m*- „ , 130.
„ „ -*p*- „ , chloride, hydroxide, 131.
Acetylene, interaction with mercuric salts, *186*, *187*.
"Acetylene mercury," 186.
„ „ oxychloride, 186.
„ tetrabromide, interaction with mercuric cyanide, 189.
Acid anilides, mercuration of, 124.
Acrylic acid, „ „ , 66.
Aldehydes, mercuration of aliphatic, 53.
Aliphatic acids, unsaturated, mercuration of, 66.
Alkyl mercuric halides, electrolysis in liquid ammonia, 30, 31.
Alkyl phenols, mercuration of, 153.
Allylacetoxime, reaction with mercuric acetate, 202.
Allyl alcohol, mercuration of, 47, *50*.
p-Allyl anisole, mercury derivatives of, 143.
Allylene, interaction with mercuric salts, *187*, *188*.
Allylmercuric hydroxide and salts, *44*, *45*.
„ „ iodide, 33, *44*.
o-Allylphenol, mercuration of, 215.
1 : 8-Amidonaphthol-3 : 6-disulphonic acid (H acid), reaction with mercuric salts, 158.
1 : 8- „ „ -4 : 6- „ „ (K acid), „ „ „ , 158.
1 : 8- „ „ -4-sulphonic acid, reaction with mercuric salts, 158.
m-Aminobenzoic acid, mercury derivatives of, 172.
p- „ „ „ and esters, mercury derivatives of, *173-176*.
Aminomethane disulphonic acid, mercuration of, 68.
Aminophenols, mercuration of, 147.
o-Aminophenylmercuric acetate, 111, *116*.
o- „ „ „ , acetyl derivative, 116.

o-Aminophenylmercuric acetate, condensation with dinitrophenylpyridinium chloride, 116.
p- „ „ „ „ , *112*, 222.
p- „ „ „ „ , acetyl derivative, 113.
p- „ „ „ „ , condensation with dinitrophenylpyridinium chloride and propargyl acetal, *113*, *114*.
p-Aminophenylmercuric chloride, *115*, 116, 222.
p- „ „ „ „ , condensation products, *115*, *116*.
p- „ „ „ hydroxide and salts, *114–116*.
p- „ „ „ thiosulphate, 115, *116*.
m-Aminophenyl-trimethylammonium chloride, mercuration of, 149.
n-Amylacetylene, mercuration of, 188.
Amyl alcohol, „ „ „ , 47.
iso-Amyl hydroxymercuri-*aci*-nitro-acetate anhydride, 64.
n-Amylmercuric bromide, 44.
tert.- „ „ „ , 30, *44*.
iso- „ „ chloride, 38, *44*, 87, 360.
iso- „ „ iodide, 38, *44*.
iso-Amylphenol, mercuration of, 153.
4 : 5-Anhydro-3-acetoxymercuri-5-hydroxymercuri-4-hydroxybenzaldehyde, 194.
2 : 3- „ -2 : 6-dihydroxymercuri-4-nitro-3-hydroxybenzaldehyde, 195.
„ -2-hydroxy-3-hydroxymercuri-5-methylazobenzene-2′-carboxylic acid, 206.
„ „ „ „ „ „ „ 4′- „ „ , 206.
„ -*α*-hydroxy-mercuribenzoyl acetic acid, 63.
„ -*α*-hydroxymercuri-*α*-hydroxymethyl succinic acid, derivatives of, 67.
Anilines, halogenated, mercuration of, 117.
α-Anilido fatty acids and esters, mercuration of, 126.
Anisole, mercuration of, 137, *141*.
Anisylindole, mercuration of, 214.
p-Anisylmercuric chloride, 87, *140*, 230.
p- „ „ oxide, 142.
Anthranilic esters, mercuration of, *160*, *168–171*.
Apiol, mercuration of, 137, *155*.
iso-Apiol, „ of, 137.
Aromatic acids, mercuration of, 160.
„ nitro compounds, mercuration of, *104–105*.
„ sulphonic acids, „ „ , *108*, *109*.
Aryl hydroxy-fatty acids, „ „ , 68.
Aryloxy-fatty acids, „ „ , 191.
Azo compounds, mercurated, *203–205*.
Behenolic esters, mercuration of, 68.
Benzalacetophenone, „ „ , 196.
Benzeneazophenol, „ „ , 203.
Benzeneazo-*p*-cresol, „ „ , 204.
Benzene sulphonic acid, mercuration of, 109.
Benzidene, „ „ , 132.
Benzoic acid, „ „ , 160, *162*.
Benzophenone, „ „ , 197.
Benzoylacetic acid, „ „ , 63.
m-Benzoylaminobenzoic acid, mercuration of, 173.
Benzoylmethyl-mercuric chloride, 63.
p-Benzylaminophenylmercuric acetate, chloride, hydroxide, nitrate, 124.
Benzylaniline, mercuration of, 124.
Benzylmercuric acetate, 95.
„ „ bromide, iodide, 86, *95*.
„ „ chloride, 80, 85, 87, *94*.
„ „ cyanide, 95.
„ „ ethyl xanthate, 191.
Benzyl mercury compounds, 79, 80, 94, 95.
p-Bismercurianiline, 222.
p-Bromodimethylaniline, mercuration of, 111, *122*.
4-Bromo-4-hydroxy-3-acetoxymercuri-1-triacetoxymercuriphenyl-2 : 3-dimethyl-5-pyrazolone, chloride, hydroxide, 212.
Bromomercuri acetic acid, 58.
o-Bromomercuri benzophenone, 198.
5- „ „ -2-bromothiophene, 99.

DropBooks

α-Bromomercuri camphor, iodide, 200.
5- ,, ,, -2-chlorothiophene, 99.
5- ,, ,, -2 : 4-diphenyl-selenophene, 217.
α- ,, ,, -*β*-ethoxy-*β*-phenylpropiophenone, 197.
,, ,, -ethyl methyl ether, chloride, iodide, sulphide, 184.
2- ,, ,, -3-hydroxy-tetrahydronaphthalene, 103.
5- ,, ,, -2-iodothiophene, 99.
α- ,, ,, -*β*-methoxy-*β*-phenylpropiophenone, 197.
1- ,, ,, methyl-4-bromo-1 : 2-dihydrobenzofurane, 216.
5- ,, ,, -2-methylthiophene, 101.
4- ,, ,, -2-nitrotoluene, 107.
2- ,, ,, thiophene, 98.
4-Bromo-1-phenyl-2 : 3-dimethyl-5-pyrazolone, mercuration of, 212.
o-Bromophenylmercuric acetate, chloride, 104.
m- ,, ,, ,, ,, , 104.
p- ,, ,, ,, ,, , 104.
Butanol mercuric chloride, bromide, 185.
Butene mercuric iodide, 185.
tert.-Butylacetylene, mercuration of, 188.
*Iso*butylene, interaction with mercuric salts, 185.
iso-Butyl hydroxymercuri-*aci*-nitro-acetate anhydride, 64.
n-Butylmercuric bromide, iodide, 43.
,, ,, ,, chloride, *43*, 87.
,, ,, ,, ethyl xanthate, 191.
iso- ,, ,, hydroxide and salts, 43.
sec.- ,, ,, chloride, 43.
,, ,, ,, bromide, 30, *43*.
,, ,, ,, iodide, 38, *43*.
tert.- ,, ,, *bromide, 30, 43.*
tert.-Butylphenol, mercuration of, 153.
Camphene, mercuration of, 200.
Camphor, ,, ,, , *195–200*.
Camphor carboxylic acid, mercuration of, 200.
Cane sugar, mercuration of, 47, 50.
Cellulose, ,, ,, , 47.
Carbon disulphide, reaction with alkyl or aryl mercuric hydroxides, 190.
Carvacrol, mercuration of, 137, *152*.
Carvacrolaldehyde, mercuration of, 152.
Chaulmoogric acid, ,, ,, , 68.
5-Chloro-4-acetoxymercuri-1-phenyl-3-methylpyrazolone, dichloride, 213.
o-Chloroaniline, mercuration of, 117.
m- ,, ,, ,, ,, , 118.
p- ,, ,, ,, ,, , 118.
Chloratodimercuracetaldehyde, 53.
Chloratotrimercuriacetaldehyde, 53, *187*.
Chloromercuri-aceto-*o*-toluidide, 130.
2-Chloromercuri-2-acetyl-indandione, 198.
,, ,, -*p*-aminobenzoic acid, 174.
,, ,, amyloxy-dicyclopentadiene, 190.
5- ,, ,, -2-*iso*amylthiophene, 100.
o- ,, ,, anisole, bromide, 141 ; iodide, 137.
p- ,, ,, ,, , 137, *142* ; bromide, iodide, 142.
,, ,, -anthranilic methyl ester, 169 ; bromide, iodide, 170.
o- ,, ,, benzoic acid, sodium salt, 161, *163*.
p- ,, ,, ,, ,, , 161, 162, *163*, 164 ; bromide, iodide, 163, 164.
p- ,, ,, ,, ,, , acid chloride, *n*-butyl ester, 164.
o- ,, ,, benzoic methyl ester, 162, *164*.
o- ,, ,, benzophenone, 197.
o- ,, ,, benzoyl chloride, 162, *164*, 165.
5- ,, ,, -2-benzylthiophene, 70, 83, *101*.
o- ,, ,, -*p*-bromodimethylaniline, bromide, formate, hydroxide, iodide, thiocyanate, 123.
5- ,, ,, -2-bromothiophene, bromide, iodide, 99.
α- ,, ,, camphor, 199.
2- ,, ,, -2-carbethoxy-Indandione, 198.
5- ,, ,, -2-carboxyl-thiophene, 99.

p-Chloromercuri-*o*-chloroaniline, 119.
o- „ „ -*p*- „ „ , 118.
5- „ „ -2-chlorothiophene, bromide, iodide, 98.
„ „ -*p*-cresol, 137, *150*.
„ „ „ „ , benzoyl derivative, iodide, 150.
„ „ „ „ methyl ether, 151.
6- „ „ -2 : 4-dichloroaniline and acetyl derivative, 118.
3- „ „ -2 : 5-dimethylthiophene, 70, 84, *102*.
2- „ „ -3 : 4- „ „ , 102.
5- „ „ -2 : 3- „ „ , 102.
5- „ „ -2 : 4- „ „ , 102.
5- „ „ -2 : 4-diphenyl-selenophene, 217.
3- „ „ -2 5- „ thiophene, 103.
„ „ ethoxy dicylopentadiene, 190.
5- „ „ -2-ethylthiophene, 101.
3- „ „ -2-hydroxy-2 : 3-dihydro-2 : 5-dimethylthiophene mercuric chloride, 101.
5- „ „ -4-hydroxy-4 : 5-dihydro-2 : 4- „ „ „ „ 102.
5- „ „ -4-hydroxy-3-methyl-6-isopropylbenzaldehyde, acetate, 153.
3- „ „ -*m*-hydroxyphenyl-trimethylammonium anhydride, 148.
3- „ „ -*p*- „ „ „ acetate, 148.
2- „ „ indandione, 198.
2- „ „ -5-iodothiophene, 83.
5- „ „ -2- „ „ , bromide, iodide, 99.
3- „ „ -4-methoxy-1-dichloromercuriphenyl-2 : 3-dimethyl-5-pyrazolone, 211.
3- „ „ -4-methoxy-1-dichloromercuriphenyl-3-methyl-2-ethyl-5- „ 211.
„ „ methoxy dicyclopentadiene, 190.
1-Chloromercurimethyl-4-bromo-1 : 2-dihydrobenzofurane, 216.
1- „ „ -6-carbomethoxy-1 : 2-dihydrobenzofurane, 216.
1- „ „ -4-carboxy-1 : 2- „ „ , 216.
1- „ „ -6- „ 1 : 2- „ „ , 216.
1- „ „ -4-carboxyvinylene-1 : 2- „ „ , 216.
(Chloromercuri methyl)-ethyl phenyl carbinol, 196.
1-Chloromercurimethyl-6-methyl-1 : 2-dihydrobenzofurane, 216.
1- „ „ -5- „ „ „ „ , 216.
1- „ „ -4- „ „ „ „ , 216.
?- „ „ -2-methyl thiophene, 99.
?- „ „ -3- „ „ , 99.
1- „ „ -β-naphthol, 158.
5- „ „ -3-nitro-4-hydroxybenzaldehyde, 194.
„ „ -4- „ -3- „ „ , 195.
„ „ -2- „ -3- „ „ , 195.
4- „ „ -2-nitrophenol, 144.
2- „ „ -4- „ , 145.
6- „ „ -2- „ , 145.
4- „ „ -2-nitroresorcinol, 156.
3- „ „ -5-nitrosalicylal aniline, 193.
3- „ „ -5-nitrosalicylic acid, 168.
4- „ „ -2-nitrotoluene, 107.
6- „ „ -2- „ „ , 107.
5- „ „ -2- „ „ , 107.
5- „ „ -3- „ „ , 108.
4- „ „ -3- „ „ , 108.
6- „ „ -3- „ „ , 108.
2- „ „ -4- „ „ , 108.
3- „ „ -4- „ „ , 108.
p-Chloromercuri phenetole, iodide, 137, *143*; bromide, oxide, 143.
o-Chloromercuri phenol, 137, *139*, 140, 141.
„ „ „ , acetyl derivative, 139.
„ „ „ , sodium salt, 137, *140*.
(2-Chloromercuriphenyl-α-amino) propionic ethyl ester, 127.
2-Chloromercuriphenylglycine ethyl ester, bromide, iodide, 127.
5-Chloromercuri-2-phenyl thiophene, 99.

DropBooks

5-Chloromercuri-2-*n*-propyl thiophene, 100.
?- „ „ -3-*iso*propyl „ , 100.
„ „ resorcinol, 138, *155*.
3(?)- „ „ salicylaldehyde, 193.
3(?)- „ „ salicylal aniline, 193.
3- „ „ salicylic acid, salts, bromide, iodide, 166.
3- „ „ „ methyl ester, 167.
o- „ „ thiolbenzoic acid and ethyl ester, 165.
2- „ „ thiophene, 70, 83, *97*, 98, 222.
5- „ „ -*o*-toluidine, diacetyl derivative, 129.
Chloromercuri thymol, sodium salt, 151.
o-Chlorophenylglycollic acid, mercuration of, 191.
o-Chlorophenylmercuric acetate, chloride, 104.
m- „ „ „ „ , 104.
p- „ „ „ , 104.
p- „ „ chloride, 78, *104*.
5-Chloro-1-phenyl-3-methylpyrazolone, mercuration of, 213.
2-Chlorotoluene-5-sulphonic acid, mercuration of, 109.
Cinnamic acid, mercuration of, 161, *176*.
Citraconic acid, „ „ , 67.
α-Cravoxy-propionic acid, mercuration of, 191.
o-Cresol „ „ „ „ , 137, *149*.
p- „ „ „ „ , 137, 149.
p- „ methyl ether, mercuration of, 137; *150*.
Crotonic acid, mercuration of, 67.
Cumylmercuric chloride, 95.
Cyanoacetic acid and esters, mercuration of, 62.
5-Cyanomercuri methyl-2 : 4-diphenyl-selenophene, 217.
1- „ „ „ -1 : 2-dihydrobenzofurane, 217.
1-Cyanomercurimethyl-4-methyl-1 : 2-dihydrobenzofurane, 217.
Cyanomercuri-salicylic acid, 168.
Cyclohexenecarboxylic ester, mercuration of, 68.
Cyclohexylmercuric bromide, 95.
„ „ chloride, 87, *95*.
„ „ cyanide, iodide, sulphide, 96.
„ mercury compounds, 81, 95, 96.
Cyclomercuri pentamethylene, 208.
Cyclomercuri polymethylenes, 208–210.
Cyclopentadiene, reaction with mercuric chloride, 190.
Diacetoxymercuri-aceto-*o*-toluidide, chloride, bromide, iodide, 130.
„ „ „ -*m*- „ 131.
2 : 5- „ „ „ -*m*- „ 131.
N-*iso*Diacetoxymercuri-*p*-aminobenzoic ethyl ester, 162, *173*, 174.
Diacetoxymercuri-p-aminobenzoic acid ethyl ester. dichloride, acetyl derivative, 176.
(2 : 4- „ „ -α-amino) propionic ethyl ester, 127.
2 : 6- „ „ -*p*-*iso*amylphenol, 153.
2 : 4- „ „ aniline and acetyl derivative, *116*, *117*.
2 : 4- „ „ anisole, 142.
N-*iso*Diacetoxymercuri-anthranilic methyl ester, 162, *168*.
2 : 4-Diacetoxymercuri-anthranilic methyl ester, 169.
2 : 6- „ „ -*p*-*tert*.-butylphenol, 153.
„ „ carvacrol, 152.
4 : 6- „ „ -*o*-chloroaniline, 117.
4 : 5- „ „ -*o*- „ „ and acetyl derivative, *117*, *118*.
2 : 6- „ „ -*p*-cresol, 149.
2 : 6- „ „ -*p*- „ compound with diazotised sulphanilic acid, 206.
4 : 6- „ „ -*o*-cresol, chloride, nitrate, 149.
„ „ -*o*-cresolphthalein, 207.
3 . 5- „ „ dimercuri-4-hydroxybenzaldehyde, 194.
„ „ „ -2-nitro-3-hydroxybenzaldehyde, 195.
3 : 4- „ „ -4-ethoxy-1-diacetoxymercuriphenyl-2 : 3-dimethyl-5-pyrazalone, 211.
4 : 6- „ „ guaiacol and derivatives, 154.
2 : 6- „ „ -*p*-hydroxyphenyl-trimethylammonium acetate, 148.
3 : 4- „ „ -4-methoxy-1-diacetoxymercuriphenyl-2 : 3-dimethyl-5-pyrazolone, 210.

3 : 4-Diacetoxymercuri-4-methoxy-1-diacetoxymercuriphenyl-3-methyl-2-ethyl-5-pyrazolone, 211.
3 : 4- „ „ -4-methoxy-1-acetoxymercuriphenyl - 3 - methyl - 5 - pyrazolone and dichloro compound, 212.
3- „ „ -4-methoxy-1-diacetoxymercuriphenyl - 3 - methyl - 5 - pyrazolone, 212.
3 : 4- „ „ -4-methoxy-1-[diacetoxymercuri-*o*-tolyl]-3-methyl - 2 - ethyl-pyrazolone, 211.
3 : 4- „ , -4-methoxy-1-[diacetoxymercuri-*p*-tolyl]-2 : 3-dimethyl-5-pyrazolone, 211.
„ „ -*N*-methylthiodiphenylamine, 126.
2 : 4- „ „ -α-naphthol, 138, *157*.
2 : 4- „ „ -α-naphthylamine, 111, *132*.
o-*p*- „ „ -*m*-nitroaniline, and acetyl derivative, 119.
2 : 6- „ „ -*p*- „ „ , 120.
„ „ -5-nitrosalicylic acid, 168.
2 : 4-Diacetoxymercuri phenetole, 144.
„ „ phenol, dichloride, 140.
(2 : 4-Diacetoxymercuriphenyl-α-amino) butyric ethyl ester, dichloride, dibromide, di-iodide, 128.
(„ „ „ „) *iso*valerianic ethyl ester, 128.
4 : 6-Diacetoxymercuri resorcinol dimethyl ether, 138, *156*.
2 : 5- „ „ salicylal aniline, 193.
3 : 5- „ „ salicylaldehyde, 192.
2 : 5- „ „ thiophene, 98.
2 : 6- „ „ thymol, sodium salt, anhydride, hydroxide, chloride, nitrate, 151.
„ „ -*o*-toluidine, 129.
2 : 5- „ „ -*m*- „ , hydroxide, chloride, bromide, 130.
„ „ -*m*- „ „ „ „ , 130.
„ „ -*o*-tolylglycine ethyl ester, 129.
„ „ -2 : 4 : 6-tribromobenzeneazo-phenol, 203.
Diallyl barbituric acid, mercuration of, 68.
Diazo-acetic esters, „ „, 65.
Dibenzalacetone, „ „, 197.
Dibromoethylene, reaction with mercuric cyanide, 188.
Dibromofluorescein, mercuration of, 208.
Dibromomercuri-di-*iso*propyl ether, iodide, 185.
2 : 4-Dichloroaniline, mercuration of, 118.
2 : 5-Dichlorobenzene sulphonic acid, mercuration of, 109.
3 : 5-Dichlorodimercuri-4-hydroxybenzaldehyde, 194.
2 : 6- „ „ -4-nitro-3-hydroxybenzaldehyde, 195.
Syn.-Dichloroethylene, reaction with mercuric cyanide, 188.
(4 : 6) ?-Dichloromercuri-*m*-aminophenyl-trimethylammonium acetate, 149.
„ „ benzophenone, 198.
4 : 6- „ „ -*o*-chloraniline and acetyl deriv., 117.
4 : 5- „ „ -*o*- „ „ , 118.
„ „ cyclopentadiene, 190.
2 : 5- „ „ 3 : 4-dimethylthiophene, 85, *102*.
2 : 5- „ „ 3-ethylthiophene, 85.
„ „ fluorescein, 208.
3 : 5- „ „ -*o*-hydroxyphenyl-trimethylammonium anhydride, 148.
(2 : 4- „ „ phenyl-α-amino) propionic ethyl ester, 128.
3 : 5- „ „ pyridine, 213.
„ „ resorcinol, 138, *156*.
2 : 5- „ „ thiophene, 84. *98*.
„ „ „ „ , reactions of, 70.
Dichloromonohydroxy-trimercuri-acetic acid, 188.
Dicyclopentadiene, reaction with mercuric chloride, 190.
p-Diethylaminophenylmercuric acetate, chloride, oxide, hydroxide, quaternary ammonium compound, 124.
Diethylaniline, mercuration of, 124.
Diethyl diallylmalonate, mercuration of, 68.
Diethyl *o*-phenylenediacrylate, mercuration of, 68.
2 : 6-Diformoxydimercuri-4-nitro-3-hydroxybenzaldehyde, 195.
3 : 5-Dihydroxydimercuri-4-hydroxybenzaldehyde, 194.
2 : 6- „ -4-imino-dihydropyrimidine-3-acetic acid, mercuration of, 192.

DropBooks

Dihydronaphthalene, mercuration of, 103.
Dihydroxybenzofurane, mercury derivatives of, 215.
2 : 4-Dihydroxymercuri aniline, 117.
„ „ -anthranilic anhydride, 170.
4 : 6- „ „ -*o*-chloroaniline, 117.
4 : 5 „ „ -*o*- „ „ 118.
„ „ -dihydroxyazobenzene sulphonic acid, 204.
„ „ fluorescein, 207.
„ „ hydroxyazobenzene sulphonic acid, 204.
„ „ -iodomercuri acetic acid and derivatives, 61.
„ „ -β-naphthol-azobenzene sulphonic acid, 204.
(2 : 4-Dihydroxymercuriphenyl-α-amino) butyric anhydride, 128.
(„ „ „ „ „) proplonic „ , 128.
Dihydroxymercuri-*o*-toluidine, acetate, chloride, bromide, iodide, acetotoluidide, 130.
1 : 8-Dihydroxynaphthalene-3 : 6-disulphonic acid, reaction with mercuric salts, 158.
$\alpha\alpha$-Di-iodomercuri camphor, 198.
β-Dimethylaminonaphthalene-6-sulphonic acid, reaction with mercuric acetate, 134.
m-Dimethylaminophenol, 137, *147*.
m-Dimethylaminophenyl acetate, 147.
p-Dimethylaminophenylmercuric acetate, methiodide, methochloride, 121.
„ „ „ „ , quaternary ammonium compound, 121.
„ „ „ chloride, 111, *121*, 122.
„ „ „ hydroxide, *121*, 122.
Dimethylaniline, mercuration of, 121.
„ anthranilic methyl ester, mercuration of, 172.
Dimethylheptenol, mercuration of, 201.
4 : 6-Dimercuri-bis-o-chloroaniline, 117.
4 : 5- „ „ „ , 118.
Dimercurimethylene iodide, 40, *45*.
Dimercury-bis-diphenyl, 81.
„ -3 : 3′(or 4′)-diethyl-2 : 2′ : 5 : 5′-dithienylene, 85.
„ -2 : 2′-5 : 5′-dithienylene, 84.
„ -3 : 4 : 3′ : 4′-tetramethyl-2 : 2′ : 5 : 5′-dithienylene, 85.
2 : 4-Dinitrodimercuribenzylidene oxide, 107.
4 : 6-Dinitrophenol, mercuration of, 136, *146*.
Diphenic acid, mercuration of, 68.
Diphenyl, mercury derivatives of, 81.
Diphenylamine, mercuration of, 125.
Di(phenylmercuri)-amine, compounds of, *91*, *92*.
Diphenylmethyl ketone, mercuration of, 196.
2 : 4-Diphenyl-selenophene, mercury derivatives of, 217.
2 : 4-Dipropionoxydimercuri-6-nitro-3-hydroxybenzaldehyde, 195.
Dipropylene oxide dimercuric hydroxide and salts, *51*, *52*.
Ethane hexamercarbide, *47*, 50, 53.
„ „ „ , dihalides, perchlorate, dinitrate, sulphate, picrate, 48.
„ „ „ hexachloride, hexa-iodide, *48*, *49*.
Ethanol mercuric chloride, sulphide, sulphate, *181*, *182*.
„ „ bromide, 58, *181*.
Ethene mercuric iodide, hydroxide, anhydride, nitrate, sulphide, 182.
Ethyl acetoxymercuri-ethoxy-chaulmoograte, 68.
Ethyl alcohol, mercuration of, 47.
p-Ethylaminophenylmercuric acetate, chloride, 123.
„ „ hydroxide, quaternary ammonium compound, 123.
Ethylanthranilic ethyl ester, mercuration of, 172.
Ethyl *n*-butylacetylene, mercury derivatives of, 188.
Ethyl chloromercuri-*aci*-nitro-acetate, 63.
Ethyl diallyl acetate, mercuration of, 68.
Ethyl diphenylamine-2-carboxylate, mercuration of, 68.
Ethylene, reaction with mercuric salts, 181–184.
Ethyl ether mercuric chloride, carbonate, 182.
„ „ „ bromide, 183.
Ethylhexenol, mercuration of, 203.
Ethyl hydroxymercuri-*aci*-nitro-acetate anhydride, 63.
Ethyl hydrazinecarboxylate, mercuration of, 191.

Ethyl mercuric ethyl xanthate, 191.
,, ,, acetate, bromide, 34.
,, ,, chloride, 33, 35, *41*, 42, 87.
,, ,, hydroxide, 35, *41*, 42.
,, ,, iodide, 21, 30, 33, 35, *42*.
,, ,, 2 : 4 : 6-trinitrophenyl, 42.
Ethyl propyl acetylene, mercury derivatives of, 188.
Ethyl thiomercuric chloride, 88.
Eugenol methyl ether, mercuration of, 137, *155*.
Fluorescein, mercury derivatives of, 207.
Formic acid. ,, ,, ,, , 58.
Furane, mercuration of, 213.
Guaiacol, mercuration of, 154.
α-Guaiacol-propionic acid, mercuration of, 191.
4-Halidemercuri-2-nitrophenols, 145.
6- ,, ,, -2- ,, , 145.
Halogenated benzenes, mercuration of, 104.
n-Heptylmercuric bromide, 44.
n-Hexylmercuric bromide, 44.
2 : 4 : 6 : 2′ : 4′ : 6′-Hexanitrodiphenyl, reaction with mercuric chloride, 105.
Hydrazines, mercuration of, *191*, *192*.
2-Hydroxy-3-acetoxymercuric-5-*iso*amylbenzaldehyde, 196.
2- ,, -3- ,, ,, -5-*tert*.-butylbenzaldehyde, 195.
4- ,, -3- ,, ,, -1-triacetoxymercuri-phenyl-2 : 3 : 4-trimethyl-5-pyrazolone, 212.
2- ,, -5-*iso*amylbenzaldehyde, mercuration of, 196.
Hydroxyazobenzenes, mercury derivatives of, *205*, *206*.
3-Hydroxybenzaldehyde, mercuration of, 193.
p- ,, ,, ,, ,, , 194.
3-Hydroxy-5-*tert*.-butylbenzaldehyde, mercuration of, 195.
4- ,, -3-chloromercuri-1-trichloromercuriphenyl-2 : 3 : 4-trimethyl-5-pyrazolone, 212.
Hydroxydimercuri-acetic acid and derivatives, 59.
Hydroxymercuri-acetic acid, anhydride of, salts of, *59*, *60*.
Hydroxymercuri-aceto-*p*-toluidide anhydride, 131.
,, ,, -acetoxymercuri-benzeneazo-phenol anhydride, 203.
,, ,, ,, ,, -4-nitro-3-hydroxybenzaldehyde, 195.
,, ,, ,, ,, -2- ,, -3- ,, ,, 195.
5- ,, ,, -2- ,, ,, -thiophene, 101.
,, ,, -*p*-aminobenzoic anhydride, 162, *175*.
3- ,, ,, -2-anisylindole, 214.
,, ,, anthranilic anhydride, 170.
o- ,, ,, benzoic acid, anhydride of, *162*, 164.
,, ,, ,, ,, ,, , salts of, 163.
3- ,, ,, -2-carboxyl-1-methylindole, 214.
p- ,, ,, *o*-chloroaniline, 117.
o- ,, ,, -*p*- ,, ,, , 118.
,, ,, cyanoacetic acid, salts, ethyl and methyl ester, 62.
,, ,, diacetoxymercuri acetic acid, anhydride of, 60.
,, ,, ,, ,, ,, ,, , nitro-acetate from, 60.
,, ,, -dibromofluorescein, 208.
6- ,, ,, -2 : 4-dichloroaniline, 118.
2- ,, ,, -4 : 6-dinitrophenol and sodium salt, 146.
,, ,, -ethoxy-chaulmoogric acid, anhydride of, 68.
,, ,, ethyl malonic methyl ester, 66.
,, ,, fluorescein, 207.
α- ,, ,, -β-hydroxy-*n*-butyric acid, anhydride of, 67.
,, ,, ,, -β-hydroxypropionic acid, anhydride of, 66.
,, ,, ,, -β-hydroxy-β-phenylpropionic acid, anhydride of, 162, *176*.
,, ,, -2-hydroxyquinoline-8-carboxylic acid, 214.
,, ,, -8- ,, ,, -5-sulphonic acid, 215.
4- ,, ,, -*o*-iodoaniline, 118.
2- ,, ,, -*p*- ,, , 118.
α- ,, ,, -β-methoxy-β-phenylpropionic acid, anhydride of, 162, *177*, 178.
,, ,, -methylanthranilic anhydride, 171.

1-Hydroxymercurimethyl-1 : 2-dihydrobenzofurane, 216.
1- „ „ „ -6-methyl-1 : 2-dihydrobenzofurane, 217.
1- „ „ „ -4- „ -1 : 2 „ „ „ , 217.
Hydroxymercuri methyl malonic ester, 65.
„ „ „ -, methyl ester, 65.
2- „ „ -naphthionic acid, sodium salt, 134.
o- „ „ -*p*-nitrobenzoic acid, 161, *165*.
3- „ „ -4-*aci*-nitro-2 : 6-dinitrophenol, anhydride and derivatives, *146*, *147*.
5- „ „ -3-nitro-4-hydroxybenzaldehyde, 194.
4- „ „ -2-nitrophenol and sodium salt, 144.
4- „ „ -2-*aci*-nitrophenol, anhydride of, 144.
2- „ „ -4-*aci*- „ , anhydride of, pyridine double salt, 145.
2- „ „ -4-nitrophenol, sodium salt, 145.
2- „ „ -4-*aci*-nitro-6-nitrophenol, anhydride, and derivatives, 146.
„ „ phenolphthalein, 207.
2- „ „ phenylglycine anhydride, 127.
„ „ -2-phenylquinoline-4-carboxylic acid, sodium salt, 215.
α- „ „ propionic acid, anhydride of, 65.
β- „ „ „ „ „ „ , 65.
3- „ „ -salicylic acid, anhydride of, 162, *166*.
„ „ „ „ „ , ammonium salt, 166.
„ „ -salicylsulphone-phthalein, 208.
o- „ „ thiolbenzoic acid, anhydride of, 165.
„ „ -*o*-tolylglycine anhydride, 129.
4-Hydroxy-2-methyl-5-*iso*propylbenzaldehyde, mercuration of, 152.
4- „ -3- „ -6- „ „ „ „ , 153.
β-Hydroxynaphthoic acid, mercuration of, 161, *178*, *179*.
„ „ „ -4 : 7-disulphonic acid, mercuration of, 179.
p-Hydroxy-*m*-nitrophenyl carbinol, mercuration of, 159.
m-Hydroxyphenyl-trimethylammonium hydroxide, mercuration of, 137, *148*.
o- „ „ „ „ „ „ , 149.
8-Hydroxyquinoline, mercury derivatives of, 215.
Indandione, mercuration of, 198.
Indole, mercury derivatives of, 214.
5-Iodo-acetylguaiacol, mercuration of, 154.
o-Iodoaniline, mercuration of, 118.
p-Iodobenzene sulphonic acid, mercuration of, 109.
o-Iodomercuri anisole, 141.
„ -anthranilic acid, 170.
5- „ -2-bromothiophene, 99.
5- „ -2-chlorothiophene, 98.
α- „ cineol, 201.
3- „ -2 : 5-dimethylthiophene, 102.
2- „ -3 : 4- „ „ . 84.
5- „ -2 : 4-diphenylselenophene, 217.
5- „ -2-ethylthiophene, 101.
2- „ -3-hydroxy-tetrahydronaphthalene, 103.
4- „ -*o*-iodoaniline, 118.
2- „ -*p*- „ , 118.
5- „ -2-iodothiophene, 99.
„ -methylanthranilic acid, methyl ester, 162, *168*.
1-Iodomercurimethyl-4-bromo-1 : 2-dihydrobenzofurane, 216.
1-Iodomercurimethyl-6-methyl-1 : 2-dihydrobenzofurane, 216.
„ „ „ -5- „ „ „ „ , 216.
„ „ „ -4- „ „ „ „ , 216.
5-Iodomercuri-2-methylthiophene, 101.
4- „ -2-nitrotoluene, 107.
o- „ phenetole, 143.
3- „ pyridine, 213.
α- „ *trans*-terpineol, 201.
β- „ „ „ , 201.
2- „ thiophene, *98*, 222.
Iodomethylmercuric iodide, 45.
p-Iodophenylmercuric acetate, 104.
Itaconic acid, mercuration of, 67.

Ketones, mercuration of aliphatic, 54.
Maleic acid, mercuration of, 67.
Malonic acid and esters, mercuration of, 66.
l-Menthyl cinnamate, mercuration of, 178.
o-Mercaptomercuri benzoic acid, 163.
N-Mercuri-aniline, 113.
p-Mercuri-bis-acetanilide, 125.
„ -3-aminobenzoic acid, 173.
2 : 2′- „ -4- „ „ „ 162, *173*.
6 : 6′- „ -2- „ „ „ 172.
„ -*p*- „ „ ethyl ester, 176.
„ -2- „ „ methyl ester, 161.
2 : 2′- „ -4-aminophenol, 147.
p- „ -aniline, 114, *116*.
„ -*o*-anisole, 137, *141*.
„ -*p*- „ „ 141.
„ -anthranilic methyl ester, 171.
o- „ -benzoic acid, 164.
p- „ „ „ „ 164.
o- „ „ methyl ester, 164.
p- „ benzylaniline, 124.
„ -*p*-bromodimethylaniline, 123.
p- „ -*o*-chloroaniline, 117.
6- „ -2 : 4-dichloroaniline, 111, *118*.
p- „ -diethylaniline, 124.
„ „ „ „ „ quaternary ammonium compound, 124.
p- „ -dimethylaniline, 111, 121, *122*.
„ „ „ „ „ condensation with thionyl chloride, 122.
„ „ „ „ „ quaternary ammonium compound, 122.
„ -(dimethyl-*p*-toluidine), 132.
p- „ diphenylamine, 125.
„ (hydroxymercuri-β-naphthol-azobenzene-sulphonic acid), 204.
„ -*m*-hydroxyphenyl-trimethylammonium acetate, 148.
p- „ -methyldiphenylamine, 126.
p- „ -monoethylaniline, 123.
„ „ -monomethylaniline, 111, *121*.
o- „ -*p*-nitroaniline, 120.
„ (nitrobenzene-azosalicylic acid), 205.
o- „ -*p*-nitrobenzoic acid and sodium salt, 165.
2 : 2′- „ -4-nitrophenol, 146.
„ -*o*-phenetole, 143.
„ -*p*- „ „ 143.
„ -*o*-phenol, 137, *140*.
„ „ „ diacetate, 139.
„ -salicylic acid, 166.
„ „ „ ethyl ester, 168.
„ „ „ methyl ester, 167.
„ -*o*-thiolbenzoic acid, 161, *165*.
„ -*p*-toluidine, 131.
„ „ „ „ condensation with dinitrophenylpyridinium chloride, 131.
Mercuric alkyl xanthates, 190.
α-Mercuri camphor oxide, 200.
4 : 6- „ -*o*-chloroaniline, 117.
4 : 5- „ „ „ „ „ 118.
α- „ -di-β-anhydrohydroxy-β-phenylpropionic acid, 162, *178*.
„ diethylene oxide, 183.
1 : 1-Mercuridimethylene-bis-1 : 2-dihydrobenzofurane, 216.
1 : 1- „ „ -bis-4-methyl-1 : 2-dihydrobenzofurane, 217.
α- & β-Mercuridimethylheptanediol iodides, *201*, *202*.
Mercuri-hydroxymercuri-acetic acid, *60*, 61.
3 : 3′- „ -mercazine, 126.
Mercuriphenyl-β-naphthylamine, 133.
Mercuro-diethylene oxide, 183.
Mercury *p*-anisyl acetylide, 189.
Mercury, aromatic compounds of types, R_2Hg, $RHgR'$, RHgX, 69.
„ benzyl acetylide, 189.

Mercury, bis-aceto-diethylmethane, 65.
„ bis-acetodimethylmethane, 64.
„ bis-α-acetyl-α-ethylpropyl, 65.
„ bis-α-acetyl-α-*iso*propyl, 64.
„ bis-benzoylmethane, 63.
„ bis-diazo-acetic ethyl and methyl esters, 65.
„ -bis-3-dinitro(?)-mercazine, 126.
„ bis-diphenyl, 69, *81*.
„ bis-malonic methyl ester, 66.
β. „ bis-propionic acid, 65.
„ bromoacetylide, 188.
„ butyl *iso*amyl, 87.
„ „ phenyl, 87.
„ chloroacetylide, 188.
„ di-*iso*amyl, 25, 44, *38*, 360.
„ di-*tert.*-amyl, 29, 38.
„ 5 : 5′-di-*iso*amyl-2 : 2′-dithienyl, *83*, 100.
„ dibenzyl, 69–71, *79*, 86, 95.
„ 5 : 5′-dibenzyl-2 : 2′-dithienyl, *83*, 101.
„ 5 : 5′-dibromo-2 : 2′- „ , 83, 100.
„ di-*p*-bromophenyl, 69, 78.
„ di-*n*-butyl, 29, *37*.
„ di-*iso*butyl, 29, *37*.
„ di-*sec*-butyl, 29, 30, *37*.
„ di-*tert.*-butyl, 29, *38*.
„ 5 : 5′-dichloro-2 : 2′-dithienyl, *83*, 99, 100.
„ 5 : 5′-dichloromercuri-2 : 2′-dithienyl, 84.
„ di-*p*-chlorophenyl, 69, *78*.
„ dicumyl, 81.
„ dicyclohexyl, 69, *81*, 95.
„ diethyl, 4, 16, 21, 29, 30, *33*, 34, 41, 42, 69, 71.
„ „ , action of metals and metallic chlorides on, 30.
„ di-*n*-heptyl, 39.
„ 5 : 5′-di-iodo-2 : 2′-dithienyl, *83*, 100.
„ dimesityl, 80.
„ dimethyl, 3–5, 15, 29, *30*, 34, 39–41, 232.
„ „ , action of metals and metallic chlorides on, 30.
„ di-4-methylcyclohexyl, 81.
„ 5 : 5′-dimethyl-2 : 2′-dithienyl, *83*, 101.
„ di-α-naphthyl, 69, 70, *81*, 96, 228.
„ di-β-naphthyl, 69, *82*.
„ *o*-*o*′-dinitrodiphenyl, 105.
„ di-*o*-nitrophenyl, 69, *78*.
„ di-*n*-octyl, 30, *39*, 44.
„ di-*sec*-octyl, 29, *39*.
„ dipentamethylphenyl, 80.
„ diphenyl, 5, 6, 12, 13, 15, 16, 26, 69, 71, *72–74*, 78, 86–89, 91–93, 220, 227, 234, 235, 242, 268, 298, 324.
„ „ , reactions of, 74–77.
„ di-*n*-propyl, 29, 30, *36*, 43, 360.
„ di-*iso*propyl, 29, *37*.
„ 5 : 5′-di-*n*-propyl-2 : 2′-dithienyl, 83.
„ dipseudocumyl, 69, *80*, 95.
„ 2 : 2′-dithienyl, 70, *82*, 98, 222.
„ di-*o*-tolyl, 69, 71, *78*, 86, 93.
„ „ -*m*- „ , 69, *78*, 93.
„ „ -*p*- „ , 15, 69, *78*, 93, 94.
„ di-*o*-xylyl, 80.
„ „ -*m*- „ , 69, *80*, 228.
„ „ -*p*- „ , 80.
„ ethyl benzyl, 71, *85*, 87.
„ „ naphthyl, 29, 87.
„ „ phenyl, 71, *85*.
„ fulminate, 53.
„ hexahydrobenzyl acetylide, 189.
„ 2 : 4 : 6 : 2′ : 4′ : 6′-hexanitrodiphenyl, 78.

Mercury iodoform, 45.
,, methyl benzyl, 87.
,, ,, butyl, 87.
,, ,, cyclohexyl, 87.
,, ,, mesityl, 87.
,, ,, naphthyl, 87.
,, ,, phenyl, 87.
,, phenoxymethyl acetylide, 189.
,, phenyl acetylide, 189.
,, ,, *o*-anisyl, 87.
,, ,, benzyl, 85.
,, ,, cyclohexyl, 87.
,, ,, ethyl acetylide, 189.
,, ,, mesityl, 87.
,, ,, naphthyl, 87.
,, ,, thienyl, 86.
,, ,, *p*-tolyl, *86*, 87.
,, propyl butyl, 87.
,, 3 : 4 : 3′ : 4′-tetramethyl-2 : 2′-dithienyl, 84.
,, 3 : 5 : 3′ : 5′- ,, ,, -2 : 2′- ,, , 84.
,, 2 : 5 : 2′ : 5′- ,, ,, -3 : 3′- ,, , 84.
,, 2 : 4 : 2′ : 4′- ,, ,, -5 : 5′- ,, , 103.
,, 2 : 4 : 2′ : 4′-tetranitrodibenzyl, 80.
,, 2 : 5 : 2′ : 5′-tetraphenyl-3 : 3′-dithienyl, *84*, 103.
,, *p*-tolyl acetylide, 189.
,, *o*-tolyl benzyl, *86*, 71.
,, tribromoethylene, 189.
,, trichloroethylene, 189.
Mesitylmercuric chloride, 87, *95*.
Methine trimercuric iodide, 45.
Methyl acetylene, interaction with mercuric salts, *187*, *188*.
p-Methylaminophenylmercuric acetate, bromide, chloride, hydroxide, nitrate, sulphate, *120*, *121*.
Methylanthranilic methyl ester, mercuration of, 171.
Methyl chavicol, mercuration of, 143.
4-Methylcyclohexylmercuric chloride, bromide, cyanide, hydroxide, iodide, 96.
Methylene blue, mercuration of, 206.
Methylene dimercuric iodide, 45.
Methyl ethyl ketone, mercury derivatives of, 57.
Methylheptenone oxime, mercuration of, 202.
Methyl hydrazine carboxylate, mercuration of, 192.
N-Methylindole, mercuration of, 214.
2-Methylindole, ,, ,, , 214.
Methylketole, ,, ,, , 214.
Methylmercuric acetate, 32, *41*.
,, ,, chloride, 32, *39*, 87.
,, ,, hydroxide, *39*, 41.
,, ,, iodide, 21, 29–33, *40*, 46.
,, ,, salts, *39–41*.
,, ,, ethyl and methyl xanthate, 191.
Methylphthalylindole, mercuration of, 214.
3-Methyl-5-pyrazolone, ,, ,, , 213.
N-Methylthiodiphenylamine, mercuration of, 126.
Monoacetoxymercuri-furane, 214.
Monoalkylanilines, mercuration of, 120.
Monobromoethylene, reaction with mercuric acetate, 190.
Monochloroacetic acid, sodium salt, reaction with mercuric oxide, 62.
Monochloroacetone, reaction with mercuric sulphate, 54.
Monochloromercuri-6-nitro-3-hydroxybenzaldehyde, 195.
Monoethylaniline, mercuration of, 123.
Monoformoxymercuri-4-nitro-3-hydroxybenzaldehyde, 195.
Monomercuric methylene iodide, 45.
,, ,, chloro-iodide, 45.
Monomethylaminonaphthalene-6-sulphonic acid, reaction with mercuric acetate, 134.
Monomethylaniline, mercuration of, 120.

DropBooks

Naphthionic acid, mercuration of, 134.
α-Naphthol, mercuration of, 156.
β- „ „ „ „, 158.
„ fatty acids, mercuration of, 191.
1- „ -4-sulphonic acid, mercuration of, 157.
1- „ -5- „ „ , reaction with mercuric acetate, 157.
2- „ -6- „ „ , mercuration of, 158.
Naphthylamines, mercuration of, 132.
Naphthylamine sulphonic acids, mercuration of, *133*, *134*.
β-Naphthylamine, „ „ „ „, 111.
„ „ „ -6-sulphonic acid, mercuration of, 111, *133*.
1 : 5- „ „ -sulphonic acid, mercuration of, 111, *134*.
α-Naphthylmercuric acetate, 96.
„ „ „ bromide, 29, 33, 81, *96*.
„ „ „ butyrate, 97.
„ „ „ chloride, 71, 82, 87, *96*, 231.
„ „ „ formate, 97.
„ „ „ iodide, 82, *96*.
„ „ „ nitrate, 72, 82, *97*.
„ „ „ sulphide, thiocyanate, 97.
Naphthyl mercury compounds, 81, 82, 96, 97.
Nitrito-dimercuracetaldehyde, 53, *187*.
o-Nitro-p-acetoxymercuri dimethylaniline, chloride, 123.
p- „ -o- „ „ monoethylaniline, chloride, 123.
„ „ „ „ „ monomethylaniline, *121*, 123.
o-Nitroaniline, mercuration of, 118.
m- „ „ „ „, 119.
p- „ „ „ „, *119*, *120*.
o-Nitrobenzal dimercuric hydroxide, anhydride of, 106.
1-p-Nitrobenzatomercurimethyl-1 : 2-dihydrobenzofurane, 217.
1-p- „ „ „ -6-methyl-1 : 2-dihydrobenzofurane, 217.
Nitrobenzene, mercuration of, *104*, *105*.
m- „ „ sulphonic acid, mercuration of, 109.
Nitrobenzoic acids, mercuration of, *165*, *166*.
o-Nitrobenzylmercuric chloride, 106.
p- „ „ „ , 107.
p-Nitro-o-chloromercuri monomethylaniline, 121.
o-Nitrodimercuribenzylidene oxide and salts, 106.
3-Nitro-4-hydroxybenzaldehyde, mercuration of, 194.
6- „ -3- „ „ „ „, 194.
4- „ -3- „ „ „ „, 195.
o-Nitrophenol, mercuration of, 136, *144*.
p- „ „ „, 145.
o-Nitrophenylmercuric chloride, 104.
m- „ „ „ , 105.
p- „ „ „ , 105.
2-Nitroresorcinol, mercuration of, 156.
5-Nitrosalicylaldehyde, mercuration of, 192.
3- „ „ „ „, 192.
5-Nitrosalicylic acid, „ „, 168.
p-Nitroso-o-chloromercuri aniline, 137, *139*.
„ „ „ phenol, 137, *139*.
Nitrotoluenes, mercuration of, 72, *105–108*.
n-Octylacetylene, mercuration of, 188.
sec.-Octylmercuric bromide, 30, *44*.
n- „ „ hydroxide and salts, 44.
Olefines, mercuration of, *180–185*.
Oleic acid, ethyl ester, mercuration of, 68.
1-Oxalato-di-mercurimethyl-1 : 2-dihydrobenzofurane, 217.
Oxindone, mercury derivatives of, 198.
Penta-acetoxymercuri-acetanilide, 14, *125*.
Pentamethylene-1 : 5-dimercuri-dibromide, dichloride, dihydroxide, di-iodide, acetylide, sulphate, sulphide, *209*, *210*.
Pentamethylene-1 : 5-dimercuridiphenyl, 210.
Perchloratomercuracetaldehyde, 53, *187*.
Phenacylmercuric chloride, 63, *196*.

Phenetole, mercuration of, 137, *143*.
Phenol, „ „ „, 136, *139*.
„ disulphonic acid, mercuration of, 166.
Phenolphthalein, mercuration of, 207.
Phenylacetylene, mercury derivatives of, 189.
Phenyl *o*-chloromercuriphenyl ethyl carbinol, 197.
Phenyldimethylpyrazolone, mercuration of, 210.
Phenylethylene, mercury derivatives of, 190.
Phenylethylmethylpyrazolone, mercuration of, 211.
Phenylmercuriamine acetate, chloride, cyanamide, nitrate, sulphate, 92.
Phenylmercuric acetate, 72, 74, 75, *90*.
„ „ amine, 328.
„ „ bromide, 73. 75, *88*.
„ „ carbonate, 90.
„ „ chloride, 71, 74–77, 86, *87*.
„ „ cyanide, hydroxide, 89.
„ „ formate, 90.
„ „ iodide, 73–76, *89*.
„ „ myristate, proplonate, 91.
„ „ nitrate, 72, 75, *90*.
„ „ oxide, 75.
„ „ sulphide, 73, *91*.
„ „ thiocarbonate, thiosulphate, 73, *91*.
„ „ thiocyanate, 74, *89*.
„ „ trinitrobenzoate, 78.
Phenyl mercury compounds, 72–78, 85–92.
„ „ -2 : 4 : 6-trinitrophenyl, *78*, 88,
1-Phenyl-3-methyl-5-pyrazolone, mercuration of, 212.
1- „ -2 : 3 : 4-trimethyl-5-pyrazolone, mercuration of, 212.
Phthaleins, mercuration of, 207.
Picric acid, „ „, 137, *146*.
l-Pinene, reaction with mercuric acetate, 200.
Propanol mercuric chloride, bromide, hydrosulphide, iodide, sulphide, 185.
Propargylmercuric iodide, 45.
Proplonic acid, mercuration of, 65.
Proplonoxymercuri-4-nitro-3-hydroxybenzaldehyde, 195.
Propyl alcohol, mercuration of, 47.
Propylene, reaction with mercuric salts, *184*, *185*.
Propylene glycol mercuric bromide, iodide, 51.
iso-Propyl hydroxymercuri-*aci*-nitro-acetate anhydride, 64.
n-Propylmercuric bromide, 36, *43*.
„ „ „ chloride, 37, *43*, 87, 360.
„ „ „ ethyl xanthate, 191.
„ „ „ hydroxide and salts, 43.
iso- „ „ „ „ , 43.
Pseudocumylmercuric chloride, bromide, iodide, 95.
Purine derivatives, mercuration of, 68.
Pyrazolones, mercuration of, *210–213*.
Pyridine, „ „, 213.
Pyrimidine, reaction with mercuric oxide, 192.
Pyrrole, mercuration of, 213.
Quinoline, mercuration of, 214.
„ -8-sulphonic acid, mercuration of, 215.
Quinone-(1)-imide *aci*-(2)-nitro-(4)-mercury, 119.
Resorcinol, mercuration of, 155.
„ dimethyl ether, mercuration of, 156.
Safrol, mercuration of, 137, *154*.
iso-Safrol, reaction with mercuric acetate, 155.
Salicylaldehyde, mercuration of, *192*, *193*.
Salicyl red, mercuration of, 208.
Salicylic acid and esters, mercuration of, *166–168*.
Salicyloxy-acetic acid, mercuration of, 191.
Salicylsulphone-phthalein, mercuration of, 208.
Salicylyl alcohol (saligenin), mercuration of, 158.
Sodium anhydro-2-hydroxy-3-hydroxymercuri-5-methyl-azobenzene-4′-sulphonate, 206.

PrepBooks

Sodium *p*-bromobenzene sulphonate, mercuration of, 109.
„ ·3-chloromercuri-4-hydroxy-azobenzene-4′-sulphonate, 205.
„ -6-hydroxymercuri-2-nitrophenolate, 145.
1·Sodiumthiosulphatomercurimethyl-1 : 2·dihydrobenzofurane, 217.
„ „ „ „ ·4-methyl-1 : 2·dihydrobenzofurane, 217.
Sodium *p*-toluene sulphonate, mercuration of, 109.
Starch, mercuration of, 47, 50.
Stearolic acid ester, mercuration of, 68.
Styrol, reaction with mercuric acetate. 190.
Styryl ethyl ether, reaction with mercuric acetate, 190.
Sulphatomercuri-dimethylanthranilic acid, chloride, 172.
1 : 1-Sulphato·mercuridimethylene·bis-1 : 2·dihydrobenzofurane, 216.
o-Sulphidomercuribenzoic acid, 161, *164*.
„ „ „ „ methyl ester, 164.
o-Sulphidomercuribenzoyl chloride, 164.
Sulphidomercuri-salicylic methyl ester, 161, *167*.
Sulphonic acids, aromatic, mercuration of, *108*, *156*.
1-Tartrato·di-mercurimethyl-1 : 2-dihydrobenzofurane, 217.
Tetra-acetoxymercuri·*α*-acetonaphthalide, 133.
„ „ diacetone hydrate and salts, 55.
„ „ fluorescein, 208.
„ „ furane, 213.
2 : 2′ : 4 : 4′·Tetrachloromercuri·diphenylamine, 111, *125*.
Tetrachloromercuri·furane, 214.
Tetrahydroxymercuri fluorescein, 208.
„ „ furane, 213.
Tetramethyldiaminotriphenylmethane-azo-*o*-chloromercuriphenol, 139.
2 : 5 : 2′ : 5′-Tetramethyl·3 : 3′-dithienyl, 70.
Tetra (phenylmercuri) thiourea, 92.
5·Thiocyanatomercuri-2·*iso*amylthiophene, 100.
„ „ „ -2-bromothiophene, 100.
„ „ „ -2-chlorothiophene, 100.
3- „ „ -2 : 5-dimethylthiophene, 103.
2- „ „ -3 : 4- „ „ , 102.
5· „ „ -2 : 3- „ „ , 102.
5- „ „ -2 : 4· „ „ , 103.
3- „ „ -2 : 5-diphenylthiophene, 103.
5- „ „ -2-ethylthiophene, 101.
5- „ „ -2-iodothiophene, 100.
1-Thiocyanatomercurimethyl-1 : 2·dihydrobenzofurane, 217.
1- „ „ „ -4-methyl-1 : 2·dihydrobenzofurane, 217.
5·Thiocyanatomercuri-2-methylthiophene, 101.
2 or 5 (?)- „ „ -3- „ „ , 101.
5- „ „ ·2-*n*·propylthiophene, 100.
2- „ „ thiophene, 98.
Thiolbenzoic acid, mercuration of, 165.
Thiophene mercury compounds, 72, 82–85, 97–103.
Thiosalicylic acid, mercuration of, 165.
Thymol, „ „ , 137, *151*.
p-Thymolaldehyde, „ „ , 152.
Thymoxyacetic acid, „ 191.
p-Toluene sulphonic acid, mercuration of, 108.
o- „ „ „ „ „ , 109.
Toluidines and toluidides, „ „ , 129.
1-*p*-Tolyl-2 : 3-dimethyl-5-pyrazolone, mercuration of, 211.
1·*o*·Tolyl-3·methyl-2-ethyl-5-pyrazolone, „ „ , 211.
Tolylglycine esters, mercuration of, 128.
o-Tolylmercuric bromide, iodide, 92.
o- „ „ chloride, *92*, 229.
o- „ „ nitrate, 72, 93.
o- „ „ sulphide, 93.
m- „ „ bromide, iodide, propionate, 93.
m- „ „ chloride, 71, *93*, 229.
p- „ „ acetate, bromide, carbonate, mercaptan, 94.
p- „ „ chloride, 71, 76, 78, 86, 87, *93*, 161, 163, 230.
„ „ „ ethyl xanthate, 191.

p-Tolylmercuric iodide, 79, *94*.
,, ,, ,, methyl xanthate, 191.
,, ,, ,, nitrate, 72, *94*.
,, ,, ,, 2 : 4 : 6-trinitrobenzoate, 79, *94*.
,, ,, ,, 2 : 4 : 6-trinitrophenyl, 94.
,, Tolyl mercury 2 : 4 : 6- ,, ,, , 79.
Tolyl mercury compounds, 78, 79, 92-94.
2:4:6-Triacetoxymercuri-*m*-chloroaniline, 118.
,, ,, phenolphthalein, 207.
,, ,, -*m*-tolylglycine ethyl ester, 129.
Tribromoethylene, interaction with mercuric cyanide, 188.
Trichloroethylene, ,, ,, ,, , 185, 188.
Trichloromercuri-acetaldehyde, 186.
,, ,, -acetic acid, *61*, *188*.
,, ,, acetone, 187.
2:4:6- ,, , -*m*-chloroaniline, 118.
,, ,, -methyl ethyl ketone, 188.
Trihydroxymercuri-acetic acid, 188.
2:4:6- ,, ,, -*m*-chloroaniline, 118.
,, ,, phenolsulphone-phthalein, 207.
Trimercuri-acetic acid, 48.
,, -diacetone hydroxide and derivatives, 56, 57.
,, -dialdehyde hydroxide, 53.
2:4:6-Trinitrophenol, mercuration of, 146.
2:4:6-Trinitrophenylmercuric chloride, 78, *105*.
Triolein, mercuration of, 146.
Vanillin, mercuration of, 154.
Vinyl oxymercurochloride, 186.
m-Xylylmercuric chloride, 80, *95*.
Xylyl mercury compounds, 80.

Boron.

iso-Amyl boric acid, 224, 226.
o-Anisyl boric acid, 230.
Benzyl boric acid, 95, *231*.
,, ,, ,, , isobutyl ester, 231.
Boron *o*-anisyl dichloride, 228.
,, *p*- ,, ,, , 228.
,, diethyl chloride, 224.
,, ,, ethylate, 225.
,, ,, hydroxide, 224.
,, diphenyl bromide, 227.
,, ,, chloride, 76, 219, *227*, 228.
,, ,, fluoride, 219.
,, *α*-naphthyl dichloride, 228.
,, *β*- ,, ,, , *228*, 231, 232.
,, *o*-phenetyl dichloride, 228.
,, *p*- ,, ,, , 228.
,, phenyl dibromide, 228.
,, ,, dichloride, 227.
,, ,, difluoride, 219, *227*.
,, ,, tetrachloride, 227.
,, propyl oxide, 226.
,, pseudocumyl dibromide, 228.
,, *o*-tolyl dichloride, 228.
,, *p*- ,, dibromide, difluoride, 228.
,, tri-*iso*amyl, 224.
,, tri-*iso*butyl, 224.
,, triethyl, 219, *224*, 225.
,, ,, ammine, 224.
,, trimethyl, *223*, 224.
,, ,, ammine, 223.
,, triphenyl, 219, *226*, 227.
,, triphenyl-ammonia, methylamine, ethylamine, 226.
,, ,, -*n*-propylamine, dimethylamine, trimethylamine, 227.

DropBooks

Boron triphenyl-aniline, pyridine, quinoline, quinaldine, piperidine, phenyl hydrazine, 227.
„ tri-*n*-propyl, *224*, 225.
„ *o*-xylyl dichloride, 228
„ *m*- „ dibromide, 228.
„ „ „ dichloride, 231.
„ *p*- „ „ , 228.
p-Bromophenyl boric acid, 229.
iso-Butyl boric acid, 226.
p-Carboxy-phenyl boric acid, 230.
p-Chlorophenyl boric acid, 229.
Diethylboric acid, *224*, 225.
Diphenyl boric acid, 227, *228*.
Di-*p*-tolyl boric acid, 229.
Ethyl boric acid, mono- and diethyl esters, 225.
„ „ „ , compound with triethyl boric ester, 225.
Methyl boric acid, 225.
α-Naphthyl boric acid and salts, 231.
β- „ „ „ „ „ , 231.
β- „ „ „ „ „ , methyl ester, 231.
α-Naphthyl boron oxide, 232.
β- „ „ „ , 232.
o-Phenetyl boric acid, 230.
Phenyl boric acid, 88, 225, 228, *229*.
„ boron chloride, 76.
„ boron oxide, 231.
Propyl boric acid, 225.
o-Tolyl boric acid, 92, *229*.
m- „ „ „ , 93, *229*.
m- „ „ „ isobutyl ester, 229.
p- „ „ „ and salts, 92, *230*.
o-Tolyl boron oxide, 231.
p- „ „ „ , 231.
o-Xylyl boric acid, 231.
m- „ „ „ and diethyl ester, 231.
p- „ „ „ , 231.
o- „ boron oxide, 231.
m- „ „ „ , 231.
m- „ „ „ , acid silver salt, 231.
p- „ „ „ , 232.
p- „ „ „ , acid silver salt, 232.

Aluminium.

Aluminium alkyl iodides, compounds with amines, 233, 234.
„ diethyl iodide, 233.
„ ethyl di-iodide, 233.
„ tri-*iso*amyl, 233.
„ tri-*iso*butyl, 233.
„ triethyl, 36, *232*.
„ „ , compound with aluminium bromide, 232.
„ triethyl-etherate, 233.
„ trimethyl, 33, *232*.
„ trimethyl-etherate, 233.
„ triphenyl, 76, 220, *234*.
„ „ , compound with ether, 234.
„ tripropyl, 37, *232*.
„ tripropyl etherate, 233.
Methylene bromide or iodide, aluminium derivatives of, 220, *234*.

Indium.

Indium diphenyl chloride, 76, 220, *235*.
„ phenyl oxide, 235.

Thallium.

Thallium compounds, comparison with gold, 4.
Thallium di-*iso*amyl chloride, fluoride, 242.
„ di-*n*-butyl bromide, carbonate, chloride, fluoride, iodide, nitrate, sulphate, 242.
„ di-*iso*butyl chloride, nitrate, 242.
„ di-*sec.*-butyl chloride, nitrate, 242.
„ dicyclohexyl chloride, 243.
„ diethyl acetate, 239.
„ „ bromide, 222, *237*.
„ „ *m*-bromobenzoate, 239.
„ „ carbonate, 238.
„ „ chloride, *237*, 238, 302.
„ „ chromate, 238.
„ „ -4 : 6-dinitro-2-aminophenoxide, 240.
„ „ dinitro-*β*-naphthoxide, 241.
„ „ -2 : 4-dinitronaphthoxide-7-sulphonate, 241.
„ „ -2 : 4-dinitrophenoxide, 240.
„ „ -2 : 6- „ „ , 240.
„ „ dinitro-*o*-tolyloxide, 241.
„ „ fluoride, 237.
„ „ hexanitrodiphenylamine, 240.
„ „ *n*-hexoate, 239.
„ „ hydrogen carbonate, 238.
„ „ hydrosulphide, 238.
„ „ hydroxide, 221.
„ „ iodide, *237*, 238.
„ „ *p*-iodobenzoate, 239.
„ „ lactate, 239.
„ „ nitrate, 238.
„ „ nitrite, 238.
„ „ *p*-nitrobenzoate, 239.
„ „ *o*-nitrophenoxide, 239.
„ „ *m*- „ „ , 239.
„ „ *p*- „ „ , 239.
„ „ *α*-nitroso-*β*-naphthoxide, 241.
„ „ -4-nitrosophenoxide, 221, *240*.
„ „ -3-nitro-*o*-tolyloxide, 240.
„ „ -5- „ „ „ , 221, *241*.
„ „ -4- „ -*m*- „ , 240.
„ „ -6- „ -*m*- „ , 240.
„ „ -3- „ -*p*- „ , 240
„ „ *n*-octoate, 239.
„ „ phosphate, 238.
„ „ propionate, 239.
„ „ sulphate, 237, *238*.
„ „ thiocyanate, 238.
„ „ trichloroacetate, 239.
„ „ trinitro-*α*-naphthoxide, 241.
„ „ 2 : 4 : 6-trinitrophenoxide, 240.
„ „ trinitro-*m*-tolyloxide, 241.
„ „ valerate, 239.
„ dimethyl acetate, 237.
„ „ bromide, *235*, 236.
„ „ carbonate, 236.
„ „ chloride, 221, *235*.
„ „ chromate, 236.
„ „ -4 : 6-dinitro-2-aminophenoxide, 237.
„ „ fluoride, 235.
„ „ hydrosulphide, 236.
„ „ hydroxide, 236, 237.
„ „ iodide, *235*, 236.
„ „ nitrate, 236.
„ „ *o*-nitrophenoxide, 236.
„ „ *m*- „ „ , 221, *236*.

DropPDFBooks

Thallium dimethyl *p*-nitrophenoxide, 237.
„ „ ·3-nitro-*o*·tolyloxide, 237.
„ di-α-naphthyl bromide, 221, *243*.
„ „ „ chloride, *243*, 360.
„ diphenyl acetate, 244.
„ „ acid butyrate, 221, *244*.
„ „ „ hexoate, 221, *244*.
„ „ „ propionate, 244.
„ „ „ valerate, 244.
„ „ bromide, 242.
„ „ *o*-bromobenzoate, 244.
„ „ *m*- „ „ , 244.
„ „ *n*-butyrate, 244.
„ „ chloride, 76, 222, *242*, 245, 340, 360.
„ „ chromate, 244.
„ „ fluoride, 242.
„ „ *n*-hexoate, 244.
„ „ nitrate, *243*, 244.
„ „ nitrite, 243.
„ „ *p*·nitrobenzoate, 244.
„ „ *o*-nitrophenoxide, 244.
„ „ *p*· „ „ , 244.
„ „ α-nitroso·β-naphthoxide, 244.
„ „ *n*·octoate, 244.
„ „ oxide, *243*, 244.
„ „ pyrophosphate, 244.
„ „ trinitro-α·naphthoxide, 244.
„ „ trinitro-*m*-tolyloxide, 244.
„ di-*p*-tolyl bromide, 243.
„ „ „ chloride, 243.
„ di-*o*· „ „ , 243.
„ dipropyl bromide, hydrosulphide, hydroxide, iodide, 241.
„ „ chloride, 37, *241*.
„ di-*iso*propyl chloride, nitrate, 242.

Silicon.

*iso*Amyl silliconic acid, 259.
*iso*Amyl silicon trichloride, 254, 256.
„ „ trichlorosilicane, see *iso*Amyl silicon trichloride.
„ „ triethoxy silicon, 256.
Anhydrobisdibenzylsilicanediol, *276*, *277*.
Anhydrobisdiphenylsilicanediol, 248, *271*–274.
„ „ „ „ , crystallographic measurements of, 365.
Anhydrobisphenylethylsilicanediol, 275.
Benzyldiethylsilicol, 270.
Benzylethyl*iso*butylchlorosilicane, *267*, 281.
Benzylethyl*iso*butylsiliool, *271*, 281.
„ „ „ „ , sulphonation of, 271.
Benzylethylbutylsilicyl oxide, *280*, 281.
Benzylethyl*iso*butylsilicyl chloride, *see* Benzylethyl*iso*butylchlorosilicane.
Benzylethyldichlorosilicane, *see* Benzylethyl silicon dichloride.
Benzylethyldipropylsilicane, 264.
„ „ „ , sulphonic acid and salts, 264.
Benzylethylpropyl*iso*butylsilicane, 265.
„ „ „ „ , sulphonic acid and salts, *264*, *265*.
Benzylethylpropylchlorosilicane, 264, 265, *267*, 271, 285.
Benzylethylpropylsilicol, 265, *270*, *271*, 280.
„ „ „ , sulphonic acid and salts, *265*, *271*.
Benzylethylpropyl silicon chloride, *see* Benzylethylpropylchlorosilicane.
Benzylethylpropylsilicyl oxide, 280.
Benzylethylsilicanediol, *278*, *279*.
Benzylethyl silicon dichloride, 266–*268*, 271, 280.
Benzylethylsilicone, 270, *280*.
Benzylmethylethylpropylsilicane, 265.
„ „ „ , sulphonic acid and salts, 265.

Benzyl orthosilicic acid triethyl ester, 284.
,, *m*-silicic acid, 270.
,, silicon trichloride, 262, *269*, 270, 284.
Benzyltrichlorosilicane, *see* Benzyl silicon trichloride.
Benzyltrimethylsilicane, 262.
Bisethoxyphenyl-*p*-bromophenyldisiloxane, 363.
Bis-(triethylmonosilyl)-ether, 257.
Bis-*p*-triethylsilylbenzene, 363.
Bis-(tripropylmonosilyl)-ether, 257.
p-Bromophenyl silicon trichloride, 263, *269*.
p- ,, ,, ,, , esters derived from, 363.
p-Bromophenyltriethylsilicane, *263*, 264.
,, ,, ,, ,, , alcohols derived from, 373.
n-Butyltrichlorosilicane, 251.
iso- ,, ,, ,, , 251, *253*.
p-Chlorophenyltriethylsilicane, 263.
p-Chlorophenyltri-*n*-propylsilicane, 264.
p-Chlorophenyl-silicon trichloride, 264, 269.
Chlorotriethoxysilicon, 257.
Cyclopentamethylenesilicon dichloride, 282.
Cyclopentamethylenesilicone, 282.
Dianhydrotrisdibenzylsilicanediol, *277*, *278*.
Dianhydrotrisdiphenylsilicanediol, 248, 273, *274*.
,, ,, ,, , crystallographic measurements of, 366.
dl-Dibenzyldiethyldipropylsilicoethane, 285.
dl-Dibenzyldiethyldipropylsilicoethane, sulphonation of, 286.
,, ,, ,, ,, disulphonic acid, *l*-menthylamine salt, 286.
Dibenzylethylchlorosilicane, *266*, 268.
Dibenzylethylpropylsilicane, 264.
,, ,, ,, , sulphonic acid and salts, 264.
Dibenzylethylsilicol, 270.
Dibenzylethyl silicon chloride, *see* Dibenzylethylchlorosilicane.
Dibenzylethylsilicyl oxide, 270.
Dibenzylmethylsilicol, 270.
Dibenzylmethylsilicyl oxide, 282.
Dibenzylsilicanediol, 258, *275*, *276*.
Dibenzyl silicon dichloride, *268*, 275.
Dibenzylsilicone, 270.
Dibromoethyl-silicon dichloride, 254.
Diethylchlorosilicon ethyl ether, 256.
Diethyl silicon dichloride, 252, *253*, 258.
Diethylsilicone, 254, *258*.
Diethyl silicon oxide, 258.
Diethylcyclopentamethylenesilicane, *282*, *361*.
Dimethyldiethylsilicane, 252.
Dimethylethyl-*iso*butylsilicane, 252.
,, ,, -*n*-propylsilicane, 252.
Dimethyldipropylsilicane, 252.
Dimethyl silicon dichloride, 282.
Diphenoxydiphenylsilicane, 290.
Diphenoxyoctaphenylsilicotetrane, 290.
Diphenylchlorosilicane, *see* Diphenyl silicon dichloride.
dl-Diphenyldiethyldipropylsilicoethane, 285.
Diphenyldiethylsilicane, 263.
Diphenyldimethylsilicane, 263.
Diphenylethylchlorosilicane, *266*, 280.
Diphenylethylsilicyl chloride, *see* Diphenylethylchlorosilicane.
Diphenylethylsilicyl oxide, 280.
Diphenylmethylchlorosilicane, 266.
Diphenylmethyl silicol, 280.
Diphenylmethylsilicyl oxide, 280.
Diphenylsilicanediol, 248, 259, *271–275*, 288, 290.
,, ,, , crystallographic measurements of, 364.
Diphenyl silicon dibromide, 268.
Diphenyl silicon dichloride, 263, *267*, 268, 272, 283, 287, 290.
Diphenylsilicone, 273, *279*.

Ethyl *iso*butyl silicon chloride, 253.
„ ortho-2 : 4-dimethylsilicobenzoate, 284.
„ orthosilico-butyrate, 256.
p-Ethylphenyltriethylmonosilane, 363.
Ethyl *n*-propyl silicon chloride, 252.
Ethysiliconic acid, 258.
Ethyl silicon trichloride, *see* Ethyltrichlorosilicane.
Ethyltrichlorosilicane, 252, *254*, 266, 268.
Ethyl triethoxy silicon, *256*, 258, 259.
Ethyl trimethoxy silicon, *256*, 259.
Hexaethylsilicoethane, 259.
Hexamethylsilicoethane, 259.
Hexaphenylsilicoethane, *284*, *361*.
p-Iodophenyltriethylsilicane, 264.
Methoxyethoxysilicon dichloride, 284.
Methylethylpropylsilicol, 264.
Methyl monosilicic acid, 256.
Methylsiliconic acid, *258*, 361.
Methyl triethoxy silicon, 258.
α-Naphthyl silicon trichloride, 269.
Octaphenylcyclosilicotetrane, *288–290*.
Octaphenyldiethylsilicotetrane, 288.
Octaphenyldi-iodosilicotetrane, 287.
Octaphenylsilicotetrane oxide, *287*, 288.
Orthosilicoacetic acid triethyl ester, *256*, 258.
α-Orthosiliconaphthoic acid triethyl ester, 284.
Phenoxydiphenylsilicyl chloride, 290.
„ „ „ „ , sulphonation of, 290.
Phenoxymethoxyethoxymenthoxysilicon, 284.
Phenoxymethoxyethoxysilicon chloride, 284.
Phenoxymethoxysilicon dichloride, 284.
Phenylbenzylethylpropylsilicane, 265.
„ „ „ , sulphonic acid, 265.
Phenylbenzylsilicanediol, 279.
Phenyl-*p*-bromophenyldichloromonosilane, 363.
Phenyl-*p*-bromophenyldiethylmonosilane, 363.
Phenyldiethylsilicol, 270.
Phenyldiethylsilicyl oxide, 270.
Phenyldimethylethylsilicane, 262, *264*.
Phenylethyldipropylsilicane, 285.
Phenyl-*p*-ethylphenyldiethylmonosilane, 363.
Phenylethylpropylchlorosilicane, *267*, 270, 285.
Phenylethylpropylsilicol, 270.
Phenylethylpropyl silicon chloride, *see* Phenylethylpropylchlorosilicane.
Phenylethylsilicanediol, *275*, 278.
Phenylethyl silicon dichloride, 266–*268*, 270, 280, 285.
Phenylethylsilicone, 270, *280*.
Phenyl-metasilicic acid, 283.
Phenylmethylethylpropylsilicane, 264.
Phenylmethylethylsilicol, 270.
Phenyl silicon trichloride, 77, 262, 263, 267, *268*, 283.
Phenyltriethylsilicane, 263.
Phenyltrimethylsilicane, 262.
Propylsiliconic acid, 259.
Propyl silicon trichloride, 252, *254*, 256, 259.
„ trichlorosilicane, *see* Propyl silicon trichloride.
„ triethoxy silicon, 256.
Silico-acetic acid, 258.
Silico-benzoic acid, 283.
„ „ „ , triethyl ester, 283.
„ „ anhydride, 279.
„ -butyric acid, 259.
Silicochloroform, 250, 251.
Silicoheptyl ethyl ether, 251, *255*.
Silicohexoic acid, 259.
Silicohydrocarbon, "unsaturated," Si_4Ph_8, 287.

Silicohydrocarbon, "saturated," Si_4Ph_8, 288.
" " , $[SiPh_2]n$, 288, 289.
α-Siliconaphthoic acid, 283.
Silico-propionic acid, 258.
Silicotoluic anhydride, 279.
Silicon diethyl diethyl ether, 255, *256*, 258.
" " ether, 253.
" ethyl triethyl ester, 254.
" propyl " " , 254.
" tetraethyl ester, 256.
" tetraphenyl, *262*, 317, 340.
" triethyl ether, 255.
" " ethyl ether, *250*, 253.
Sulphobenzylethyl*iso*butylsilicyl oxide, 281.
" " " " " ; sulphonic acids and salts, *281*, *282*.
Sulphobenzylethylpropylsilicyl oxide, 280.
" " " " , sulphonic acids and salts, *280*, *281*.
Tetra-*iso*amylsilicane, 250.
Tetra-anhydrotetrakisdiphenylsilicanediol, *273*, 275, 288, 361.
" " " " , crystallographic measurements, 368.
Tetrabenzyl silicane, 262.
Tetraethoxysilicon, 256, 258.
Tetraethylsilicane, 23, *250*, 252, 253, 361.
Tetramethyl silicane, 18, *248*, 361.
Tetranitrophenyl silicane, 262.
Tetraphenyl silicane, *259*, 262, 266, 268, 361.
Tetrapropyl silicane, 24 *250*, 251.
Tetra-*m*-tolyl silicane, 262.
" -*p*- " " , 262.
Tolylsiliconic acid, 283.
p-Tolyl silicon trichloride, 269.
Tri-*iso*amylbromosilicane, *253*, 256.
Tri-*iso*amylsilicane, 251.
Tri-*iso*amylsilicol, 256.
Tri-*iso*amyl silicon bromide, *see* Tri-*iso*amylbromosilicane.
Tri-*iso*amyl silicon oxide, 250, *253*.
Trianhydrotetrakisdiphenylsilicanediol, *275*, 361.
Trianhydrotrisdibenzylsilicanediol, *276*,–*278*.
" " " , crystallographic measurements of, 369.
Trianhydrotrisdiphenylsilicanediol, *273*, 274, 290.
" " " , crystallographic measurements of, 367.
Tribenzylchlorosilicane, 266.
Tribenzylsilicol, 266, *270*.
Tri-*iso*butylbromosilicane, 253.
Tri-*iso*butylsilicane, *251*, 253.
Trichlorosilicane, 250, 251.
Trichloro-*p*-triethylsilylphenylmonosilane, 363.
Triethoxysilicon chloride, 256.
Triethylacetoxyethylsilicane, *252*.
Triethyl*iso*amylsilicane, 252.
Triethylbromosilicane, 250, 251, *253*, *363*.
Triethylbromo-*p*-phenylmonosilane, *291*, 362.
Triethyl-*n*-butylsilicane, 252.
Triethyl*iso*butylsilicane, 252.
Triethylchloroethylsilicane, 250, 252.
Triethyl-*p*-chlorophenylmonosilane, *291*, *362*.
Triethylchlorosilicane, *253*, 255.
Triethylhydroxyethylsilicane, 252.
Triethyl-*p*-iodophenylmonosilane, 362.
Triethylphenylsilicane, 362.
Tri-*n*-propyl-*p*-chlorophenylmonosilane, 362.
Triethyl-*n*-propylsilicane, 252.
Triethylsilicane, 23, *251*.
Triethylsilicol, 253, *254*, 259, *363*.
Triethyl silicon acetate, *253*, 254.
" " chloride, *see* Triethylchlorosilicane.

DropBooks

Triethyl silicon oxide, 253, *257*.
Triethylsilicyl ethyl ether, 23.
1-Triethylsilyl-4-triethylstannyl-benzene, 291.
1- „ „ -4-trimethylplumbyl-benzene, 291.
1- „ „ -4-diphenylarsyl benzene, 291.
Trimethyl*iso*amylsilicane, 252.
Trimethyl-*n*-butylsilicane, 251.
Trimethyl*iso*butylsilicane, 251.
Trimethylethylsilicane, 251.
Trimethyl-*n*-propylsilicane, 24, *251*, 253, 257.
Trimitrophenylsilicol, trisulphonate of, 269.
Triphenylbromosilicane, 263, *266*, 268, 361.
Triphenylchlorosilicane, 262, 263, *266*, 267, 269, 284.
Triphenylethylsilicane, 263.
Triphenylmethylsilicane, 262.
Triphenylsilicane, 263.
Triphenylsilicol, 262, 266, *269*, 280.
„ „ trisulphonic acid, 269.
Triphenyl silicon acetate, 266.
„ „ bromide, *see* Triphenylbromosilicane.
„ „ chloride, *see* Triphenylchlorosilicane.
„ „ oxide, 361.
Triphenylsilicylamine, 266.
Tripropylbromosilicane, *253*, 255.
Tripropylsilicane, 250, *251*.
Tripropylsilicol, 253, *255*.
Tripropyl silicon acetate, *253*, 255, 258.
„ „ bromide, 255.
„ „ oxide, 251, 253, *257*.

Germanium.

Dimethylaminophenylgermanic acid anhydride, 299.
Dimethylanilino germanium trichloride, hydrochloride of, 299.
Disodium diphenyl germamide, 296.
Germanium dimethylanilino triphenyl and hydrochloride, 298.
„ ethyl triphenyl, 298.
„ tetra-*iso*amyl, 293.
„ tetrabenzyl, 298.
„ „ tetrasulphonic acid and barium salt, 298.
„ tetra-*n*-butyl, 293.
„ tetraethyl, 291, *292*, *293*, 361.
„ tetramethyl, *291*, *292*, 361.
„ tetraphenyl, *294*, 295, *297*, 361.
„ tetrapropyl, 293.
„ tetra-*p*-tolyl, *297*, *298*
„ triphenyl anisyl, 298.
„ „ -*p*-tolyl, 298.
Hexaphenyldigermane, 294–*296*, 361.
Phenylgermamic acid anhydride, 298.
Phenylgermanonic acid, 297.
Sodium triphenyl germanide, 294, *295*, 296.
„ „ germanolate, *296*, 297.
Tetra-anhydrotetrakisdiphenylgermanediol, *297*, 361.
Tetraphenylgermane, 294.
p-Tolylgermanic acid anhydride, 299.
Trianhydrotetrakisdiphenylgermanediol, *297*, 361.
Trimethylstannyl-triphenylgermane, 296.
Triphenylgermane, 296.
Triphenylgermanol, 297.
Triphenylgermanium bromide, *294*, 296–298, 361.
„ „ chloride, 294.
„ „ fluoride, *294*, 296.
„ „ iodide, 294.
„ „ oxide, *294*, 297, 361.

Tin.

1 : 10-Bis-triethylstannyl-*n*-decane, 330.
1 : 5- „ „ -*n*-pentane, 330, *331*, *373*.
Dimethylmethylene stannane, 316.
Disodium dimethyl stannane, 313, *315*, 316.
„ diphenyl stannide, 320, 329.
„ hexamethyl tristannane, *315*, 316.
„ tetramethyl-distannane, 315.
„ tin diphenyl, *see* Disodium diphenyl stannide.
Dodecamethylpentastannane, 316.
Ethyl stannonic acid, 313.
Hexabenzyldistannane, 327.
Hexa-*iso*butyldistannane, *315*, *372*.
Hexacyclohexyldistannane, 327.
Hexaethyldistannane, 305, 306, *314*, *372*.
Hexamethyldistannane, 314.
Hexaphenyldistannane, *327*, 361.
Hexa-*n*-propyldistannane, *315*, *372*.
Hexa-*p*-tolyldistannane, 327.
Hexa-*p*-xylyldistannane, 327.
Methyl stannonic acid, *311*, 312, 361.
iso-Propyl stannonic acid, 313.
Sodium tin triphenyl, *328*, 329.
Sodium trimethyl stannide, *304*, 314.
sym.-Tetraethyldi-*iso*butyl-distannane, *315*, *372*.
sym.- „ „ -*n*-propyl- „ , *315*, *372*.
Tin di-*iso*amyl, 310.
„ dibenzyl acetate, 325.
„ „ chloride, 321, *325*.
„ „ dibromide, di-iodide, oxide, 325.
„ di-*iso*butyl salts, 310.
„ dicyclohexyl, 327.
„ dicyclohexyl dibromide, 318, *325*.
„ „ dichloride, difluoride, dihydroxide, di-iodide, *325*, *326*.
„ diethyl, 300, 301, 309, *313*, 314.
„ diethyl-*n*-amyl bromide, *331*, *373*.
„ „ *iso*-amyl bromide, 370.
„ „ „ chloride, 370.
„ „ -5-bromoamyl bromide, 329, *330*, *373*.
„ „ *iso*butyl bromide, 370.
„ „ cyclopentamethylene, 329, *330*, 361, *373*.
„ „ di-*iso*-amyl, 370.
„ „ dibenzyl, 320.
„ „ dibromide, *309*, 311, 329, 330, *371*.
„ „ di-*iso*butyl, 370.
„ „ dichloride, 302, 303, *309*, 311, 313, 360.
„ „ di-iodide, 18, 21, 302, 303, 306, *309*, 329.
„ „ oxide, *309*, 313.
„ „ *n*-propyl bromide, chloride, 370.
„ „ salts, *309–311*.
„ dimethyl, *313*, 315.
„ „ -5-bromoamyl bromide, *329*, *373*.
„ „ -cyclopentamethylene, 329, *331*, *373*.
„ „ di-*iso*butyl, 370.
„ „ diethyl, 18, *303*, 360.
„ „ dibromide, *308*, 313, 315, 316, 329.
„ „ dichloride, 303, *308*, 314.
„ „ di-iodide, *308*, 329, 371.
„ „ ethyl bromide, 303.
„ „ ethyl propyl, 303.
„ „ diphenyl, 320.
„ „ salts, *308*, *309*.
„ di-α-naphthyl, 327.
„ diphenyl, *326*, 327, *329*.
„ diphenyl aminochloride, 325.

IronBooks

Tin diphenyl chlorobromide, chloro-iodide, 324.
„ „ dibromide, 324.
„ „ dichloride, 77, 225, 322, *323*, 324, 361.
„ „ diethoxide, 324.
„ „ difluoride, 324.
„ „ hydride, 329.
„ „ hydroxychloride, *324*, 360.
„ „ oxide, 324.
„ di-*n*-propyl salts, 310.
„ di-*iso*propyl salts, 310.
„ di-*p*-tolyl, 326.
„ di-*p*-xylyl, 327.
„ ethyl butyl dibenzyl, 320.
„ „ di·*iso*amyl bromide, 370.
„ „ dibenzyl iodide, 320.
„ „ dibutyl benzyl, 320.
„ „ di·*iso*butyl bromide, 370.
„ „ phenyl dichloride, 326.
„ „ *n*·propyl di·*iso*amyl, 303.
„ „ propyl dibenzyl, 307, *320*, 321.
„ „ „ dichloride, 307.
„ „ tribromide, 313.
„ „ tri-*iso*butyl, 369.
„ „ tri-*n*·propyl, 369.
„ methyl ethyl dibromide, 303.
„ „ „ dipropyl, 303.
„ „ „ *n*-propyl *dextro*·bromocamphor sulphonate, 307, 308.
„ „ „ „ „ ·camphor sulphonate, 307.
„ „ „ iodide, 307.
„ „ sulphate (basic), 312.
„ „ tribromide, trichloride, 312.
„ „ tri-iodide, 301, 311, *312*.
„ *iso*propyl tribromide, 313.
„ „ trichloride, 313.
„ tetra·*iso*amyl, 302.
„ tetrabenzyl, 318.
„ tetrabromide, physical constants of, 371.
„ tetra·*iso*butyl, 302.
„ tetra-cyclohexyl, *317*, 323, 325.
„ tetraethyl, 21, 26, 300, *301*, 302, 305, 309, 361, *371*.
„ tetramethyl, *301*, 304, 305, 312, 315, 361.
„ tetraphenyl, 13, *316*, 321–324, 329, 360, 361.
„ tetrapropyl, 24, 37, *302*. *371*.
„ tetra·α-thienyl, 318.
„ „ -*o*-tolyl, 317.
„ „ -*m*- „ , 317.
„ „ -*m*-xylyl, 317.
„ „ -*p*- „ , 317.
„ tri·*iso*·amyl salts, 371.
„ tribenzyl chloride, 320, *323*, 325, 327.
„ „ iodide, 327.
„ „ ethyl, 320.
„ tri-*iso*butyl *iso*-amyl, 369.
„ tri-*iso*butyl salts, *306*, *307*, *371*.
„ tricyclohexyl bromide, 319, *323*.
„ „ „ chloride, 318, *323*.
„ „ „ ethyl, 320.
„ „ „ fluoride, hydroxide, iodide, 323.
„ „ „ methyl, 319.
„ „ „ phenyl, 319.
„ „ „ *p*-tolyl, 319.
„ triethyl *iso*amyl, 369.
„ „ *n*-amyl, 329, *330*, *331*, *373*.
„ „ bromide, 291, *305*, 314, 330, 331, *371*.
„ „ -5-bromoamyl, 329, *330*, *373*.
„ „ *iso*butyl, 369.

Tin triethyl carbonate, 302, *306*.
„ „ chloride, 302, *305*, 314, *371*.
„ „ ethylate, 371.
„ „ ethyl sulphonate, 302.
„ „ iodide, 18, 300–303, *305*, 309, 314, 360, *371*.
„ „ methyl, 18, *303*.
„ „ phenyl, *321*, 326.
„ „ *n*-propyl, *303*, *369*, *371*.
„ „ salts, *305*, *306*.
„ trimethyl, 304, 305, *314*.
„ „ benzyl, 321.
„ „ bromide, 296, 300, 303, *304*, 314, 321, 328.
„ „ 5-bromoamyl, 330, *331*, *373*.
„ „ chloride, fluoride, 304.
„ „ ethyl, 302.
„ „ ethylate, 305.
„ „ hydroxide, 305.
„ „ „ , electrical conductivity of solutions of, 305.
„ „ „ , complexes of, 305.
„ „ iodide, 301, 302, *304*, 321, *371*.
„ „ phenyl, 321.
„ „ *n*-propyl, 303.
„ (trimethylstannyl)-amine, 321.
„ trimethyl sulphide, formate, acetate. 305.
„ triphenyl, *328*, 361.
„ „ bromide, *322*, 327, 361.
„ „ chloride, 318, *322*, 325, 360.
„ „ cyclohexyl, 318.
„ „ ethyl, 319.
„ „ fluoride, 322.
„ „ hydride, 328.
„ „ iodide, 319, *322*.
„ „ methyl, 319.
„ „ α-naphthyl, 318.
„ „ *p*-tolyl, 318.
„ „ *p*-xylyl, 318.
„ tri-*n*-propyl *iso*butyl, 369.
„ tripropyl chloride, *306*, *371*.
„ „ iodide, 37, 302, *306*, *371*.
„ tri-*iso*propyl bromide, chloride, iodide, *306*, *371*.
„ tripropyl salts, 306.
„ tri-*iso*propyl salts, 306.
„ tri-*o*-tolyl bromide, chloride, iodide, 322.
„ „ -*p*- „ „ , *322*, 327.
„ „ „ „ chloride, fluoride, 322.
„ tri-*m*-xylyl fluoride, 322.
„ „ -*p*- „ „ , chloride, bromide, iodide, 323.
1-Triethylsilyl-4-triethylstannyl benzene, 291.
1-Trimethylstannyl-5-trimethylplumbyl-*n*-pentane, 330, *331*, *373*.
Trimethyltriethyldistannane, 314.
Triphenyltrimethyldistannane, 328.

Lead.

1 : 5-Bis-trimethylplumbyl-*n*-pentane, 330, *353*, *379*.
Lead *iso*butyl *iso*amyl dibromide, 339.
„ „ tri-*iso*amyl, 375.
„ di-*iso*amyl dibromide, dichloride, 338.
„ „ „ ethyl propyl, 377.
„ di-*iso*butyl chlorobromide, 338.
„ „ „ dibromide, dichloride, 338.
„ dicyclohexyl dibromide, 342, *348*.
„ „ „ dichloride, di-iodide, sulphide, 348.
„ diethyl *iso*amyl chloride, 339.
„ „ 5-bromoamyl bromide, 353.
„ „ *iso*butyl isoamyl, 377.

DropBooks

Lead diethylcyclopentamethylene, *352*, 353, 361, *379*.
,, diethyl di-*iso*amyl, 376.
,, ,, dibromide, 338.
,, ,, di-*iso*butyl, 376.
,, ,, dichloride, 335, *338*, 351, 352, 360.
,, ,, di-α-naphthyl, *343*, 360.
,, ,, diphenyl, 338, *343*, 360.
,, ,, di-*n*-propyl, 376.
,, ,, di-*sec.*-propyl, 376.
,, ,, methyl *iso*amyl, 377.
,, ,, ,, *iso*butyl, 377.
,, ,, ,, propyl, 377.
,, ,, propyl *iso*amyl, *336*, *377*.
,, ,, ,, *sec.*-amyl, 377.
,, ,, ,, *n*-butyl, 377.
,, ,, ,, *iso*butyl, 377.
,, ,, ,, *sec.*-butyl, 377.
,, ,, *n*-propyl *sec.*-propyl, 377.
,, , estimation of in organic compounds, 334.
,, ethyl *iso*amyl dichloride, 339.
,, ,, *iso*butyl dibromide, 339.
,, ,, -5-chloroamyl dichloride, 352, *353*.
,, ,, -*n*-propyl-*n*-butyl-*iso*amyl, 336.
,, dimethyl *sec.*-butyl *iso*amyl, 377.
,, ,, di-*iso*amyl, 376.
,, ,, dibromide, dichloride, di-iodide, oxide, sulphide, chromate, 338.
,, ,, di-*iso*butyl, 376.
,, ,, diethyl, 335.
,, ,, di-*n*-propyl, 376.
,, ,, ethyl *iso*amyl, 377.
,, ,, ,, *sec.*-amyl, 377.
,, ,, ,, *iso*butyl, 377.
,, ,, ,, *sec.*-butyl, 377.
,, ,, ,, *n*-propyl, *336*, 377.
,, ,, ,, *sec.*-propyl, 377.
,, ,, propyl *iso*-amyl, 377.
,, diphenyl, *348*, *349*.
,, ,, carbonate (basic), 346.
,, ,, chromate, 347.
,, ,, cyanide (basic), 347.
,, ,, cyclohexyl bromide, 351.
,, ,, ,, methyl, 351.
,, ,, diacetate, *346*, 347.
,, ,, dibromide, 342, 343, *345*.
,, ,, dichloride, 340, *345*, 360, 361.
,, ,, dicyanide, 347.
,, ,, dicyclohexyl, 342.
,, ,, diformate, 346.
,, ,, di-iodide, 342, *346*, 350.
,, ,, di-α-naphthyl, 342.
,, ,, dinitrate, *346*, 347.
,, ,, ,, (basic), 346.
,, ,, di-*p*-nitrobenzoate, 347.
,, ,, di-*o*-tolyl, 342.
,, ,, di-*p*-tolyl, 349.
,, ,, dithiocyanate, 347.
,, ,, di-trichloroacetate, 346.
,, ,, divalerate, 346.
,, ,, di-*p*-xylyl, *342*, 351.
,, ,, ethyl bromide, 351.
,, ,, iodate, 346.
,, ,, methyl bromide, 351.
,, ,, oxalate, 346.
,, ,, oxide, 346.
,, ,, phosphate, 346.
,, ,, propionate (acid salt), 346.

Lead diphenyl sulphide, 347.
,, ,, *p*-xylyl, 351.
,, di-*n*-propyl dichloride, 338.
,, di-*p*-tolyl diacetate, *347*, 348.
,, ,, dibromide, dichloride, 347.
,, ,, diformate, 347.
,, ,, di-iodide, *347*, 350.
,, ,, dinitrate, 347.
,, ,, sulphide, chromate, 348.
,, di-*m*-xylyl dichloride, 350, *360*.
,, di-*p*-xylyl dibromide, 345, *348*, 350.
,, ethyl tri-isoamyl, 375.
,, ,, tri-isobutyl, 375.
,, ,, tri-*n*-propyl, 375.
,, methyl ethyl dichloride, 338.
,, ,, ,, di-iodide, chromate, sulphide, 339.
,, ,, ,, *n*-propyl *iso*amyl, 336.
,, ,, ,, ,, *iso*butyl, 336.
,, ,, *n*-propyl *iso*amyl chloride, 339.
,, ,, tri-*iso*amyl, 375.
,, ,, tri-*iso*butyl, 375.
,, ,, triethyl, 334, *335*, 360, *374*.
,, ,, tri-*n*-propyl, 375.
,, phenyl cyclohexyl methyl bromide, 351.
,, *n*-propyl *iso*amyl dichloride, sulphide, 339.
,, ,, *iso*butyl dibromide, sulphide, 339.
,, ,, ,, dichloride, 339.
,, ,, tri-*iso*amyl, 375.
,, ,, tri-*iso*butyl, 375.
,, tetra-*iso*amyl, 333.
,, tetra-*iso*butyl, 333.
,, tetracyclohexyl, *341*, 348.
,, tetraethyl, 21, *333*, 360, 361.
,, tetramethyl, *333*, 336, 361.
,, tetraphenyl, 317, *339*, 340, 343–346, 360, 361.
,, tetra-*n*-propyl, 333.
,, tetra-*sec.*-propyl, 333.
,, tetra-*α*-thienyl, 341.
,, tetra-*p*-tolyl, *340*, 347,
,, tetra-*p*-xylyl, 341.
,, tri-*iso*amyl chloride, bromide, iodide, fluoride, hydroxide, 338.
,, tri-*iso*butyl *iso*amyl, 375.
,, tri-*n*-butyl chloride, bromide, hydroxide, 337.
,, tri-*iso*butyl chloride, bromide, iodide, fluoride, 337.
,, tricyclohexyl, 345.
,, ,, ,, bromide, chloride, fluoride, hydroxide, 345.
,, ,, ,, iodide, *345*, 351.
,, triethyl, 339.
,, triethyl *n*-amyl, *353*, *379*.
,, ,, *iso*amyl, *335*, *374*.
,, ,, *sec.*-amyl, 375.
,, ,, benzyl, 343, *378*.
,, ,, 5-bromoamyl, *353*, *379*.
,, ,, *iso*butyl, *335*, *374*.
,, ,, *sec.*-butyl, 375.
,, ,, bromide, iodide, 336.
,, ,, chloride, *336*, 339, 360.
,, ,, hydroxide and salts, *336*, *337*, 339.
,, ,, *α*-naphthyl, 378.
,, ,, phenyl, 378.
,, ,, *n*-propyl, *335*, *374*.
,, ,, *o*-tolyl, 378.
,, ,, *p*-tolyl, 378.
,, trimethyl *iso*amyl, *335*, *374*.
,, ,, bromide, 330, 331, 334, *336*, 353.
,, ,, *n*-butyl, *335*, *374*.

DropBooks

Lead trimethyl *iso*butyl, *335*, *374*.
„ „ chloride, 291, 334, *336*.
„ „ ethyl, *334*, 338, *374*.
„ „ fluoride, hydroxide, iodide, 336.
„ „ phenyl, 378.
„ „ *n*-propyl, *334*, *374*.
„ „ *iso*propyl, 375.
„ „ sulphate, 331, *336*.
„ „ *o*-tolyl, 378.
„ „ *p*-tolyl, 378.
„ triphenyl, *349*, 361.
„ „ bromide, 341, *344*, 351, 361.
„ „ chloride, *343*, 344.
„ „ cyclohexyl, *342*, 351.
„ „ ethyl, 351.
„ „ fluoride, 344.
„ „ iodide, 343, *344*, 349.
„ „ methyl, 351.
„ „ α-naphthyl, 342.
„ „ *p*-phenetyl, 341.
„ „ *p*-phenoxyphenyl, 342.
„ „ sulphide, 344.
„ „ *p*-tolyl, 341.
„ „ *m*-xylyl, 341.
„ „ *p*-xylyl, 341.
„ tri-*n*-propyl *iso*amyl, 375.
„ „ „ *iso*butyl, 375.
„ „ „ acetate, bromide, chloride, fluoride, hydroxide, sulphate, 337.
„ tri-*o*-tolyl, 350.
„ „ -*p*- „ , 344, *350*.
„ „ „ „ fluoride, iodide, 344.
„ tri-*m*-xylyl, *350*, 360.
„ „ -*p*- „ , 344, 345, *350*.
„ „ „ „ bromide, 341, *345*.
„ „ „ „ chloride, 344.
1-Triethylsilyl-4-trimethylplumbyl-benzene, 291.
1-Trimethylstannyl-5-trimethylplumbyl-*n*-pentane, 330, *331*, *373*.

Phosphorus.

Dimethylamidophosphenyl chloride, 122.
Diphenyl phosphorus chloride, 16.
Ethyl dichlorophosphine, 35.
Phenyl-*p*-tolylchlorophosphine, 94.
Phosphenyl chloride, 77, 94.
m-Tolyldichlorophosphine, 78.
Triethylphosphine, 20.
Trimethylphosphine, 18.
Triphenylphosphine, reaction with thallic chloride, 360.
Tripropylphosphine, 24.
m-Xylyldichlorophosphine, 80, 95.

Arsenic.

Arsenobenzene, reaction with mercury diethyl, 35.
Ethyldichloroarsine, 35.
Diphenylchloroarsine, 77, 291, 340.
Dithienylchloroarsine, 83, 98.
α-Naphthyldichloroarsine, 82.
β- „ „ „ , 82.
Phenylarsenious chloride, 77, 88, 91, 360.
„ „ oxide, reaction with mercuric chloride, 73.
„ „ sulphide, reaction with mercury diethyl, 35.
Phenyldichloroarsine, *see* Phenylarsenious chloride.
Phenyldiethylarsine, reaction with mercury diethyl, 35.
Thienyldichloroarsine, 83, 98.

Triethylarsine, 20.
1-Triethylsilyl-4-diphenylarsyl benzene, 291.
Trimethylarsine, 18.
Triphenylarsine, 226, 360.
,, ,, dichloride, 360.
Tripropylarsine, 24.
Trithienylarsine, 83.
Tri-*m*-xylylarsine, 360.
,, -*p*- ,, , 360.
m-Xylylarsenious dichloride, 80, 360.
p- ,, ,, ,, , 360.
m-Xylyldichloroarsine, *see* *m*-Xylylarsenious dichloride.

Antimony.

Diphenylstibine chloride, 340.
,, ,, trichloride, 77, 340.
Trianisylstibine mercurichloride, 142.
Triethylstibine, 20, 35.
Trimethylstibine dichloride, 32.
Triphenylstibine, 71, 88, 226, 360.
,, ,, dichloride, 77, 360.
Tri-*m*-tolylstibine mercurichloride, 71, 93.
Tri-*m*-xylylstibine, 360.
,, ,, ,, dichloride, 360.

Bismuth.

Bismuth triethyl, 34, 36.
Di-α-naphthylchlorobismuthine, 360.
Diphenylchlorobismuthine, 340, 360.
Di-*p*-tolylchlorobismuthine, 360.
Triethylbismuthine, 29, 41.
Tri-α-naphthylbismuthine, 243, 360.
Triphenylbismuthine, 77, 242, 360
Tri-*p*-tolylbismuthine, 243, 360.

DropBooks

Selenium, Tellurium.

Selenium, mercury derivatives containing, 217
Tellurium diethyl, 36.
Tellurium diphenyl, 77.
,, ,, dichloride, 340.

*

PATENT INDEX.

AMERICAN PATENTS

1074781, 191.
1259517, 207.
1457675, 68.

BRITISH PATENTS.

277 (1913), 181.
4075 (1913), 191.
161922 (1909), 168.

FRENCH PATENT.

479656, 181.

GERMAN PATENTS.

23914, 166.
30511, 168.
143448, 158.
143726, 158.
182217, 106.
182218, 106.
201903, 208.
208634, 59, 66.
213371, 59, 66.
216267, 168.
221483, 66.
224435, 168.
224491, 192.
224864, 168.
227391, 168.
228877, 68, 178.
229574, 168.
229575, 163, 168.
229781, 168.
231092, 66.
234054, 166, 172.
234851, 141, 144.
236893, 214.
245571, 68.
246207, 68.
248291, 66, 126, 168, 172, 176.
249332, 166.
249725, 173.
250746, 156.
251332, 165.
255030, 166.
261229, 191.
261875, 166, 168, 191.
264267, 68, 191.
264338, 172.
267411, 178.
267412, 178.
272289, 73.
275932, 200.
279199, 68.
279957, 178.
281009, 176.
282376, 68.
282377, 68.
286097, 207.
289246, 214.
290210, 166.
292310,
308335, 207.
371467, 227–229, 231.
407669, 166.
410969, 141, 178.
413835, 166.

SWISS PATENT.

74446, 181.

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